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PREPARATION AND ANALYSIS OF POLYSULFIDE COOKING LIQUOR

SUMMARY

A series of experiments conducted in the Institute Pulping laboratory indicated that an increase in pulp yield over kraft cooks could be realized from digestions with a polysulfide-rich alkaline liquor. This project was set up with a two-fold objective:

(1) To prepare a liquor with a minimum amount of thiosulfate (ineffective in the cooking process, yet rich in polysulfide sulfur).

(2) To set up a reliable analysis scheme for polysulfide cooking liquors and investigate methods of polysulfide sulfur analysis--in particular the work of Rene Berthier (1), Richard B. Kesler and S. T. Han (2).

Six polysulfide cooking liquors were prepared under various conditions and analyzed for sodium sulfide, sodium polysulfide, sodium sulfite, sodium thiosulfate, and gravimetric total sulfur according to the methods of Kesler and Han (2). In addition, sodium polysulfide was determined by Berthier's method (1).

Results and conclusions of this work are as follows.

(1) To realize the objective of low thiosulfate content and rich polysulfide content. The most desirable preparation found to date is to dissolve elemental sulfur in a solution of sodium sulfide, then add the caustic needed. The merit of this preparation is offset to some extent by the need for a modified recovery system.

(2) From a commercial standpoint, the most advantageous preparation would be to dissolve elemental sulfur in a solution of sodium carbonate and sodium sulfide (purified green liquor), then causticize. Although the thiosulfate content is higher than for a sodium-sulfide-plus-sulfur system, it is in turn much lower than for the usual sulfur-dissolved-in-sodium-hydroxide systems. This scheme would fit the present recovery systems.

(3) The Kesler and Han method (2) proved to be superior in both accuracy and time consumed for analysis of polysulfide cooking liquors. Only one additional titration for determination of the polysulfide sulfur was necessary. The Berthier method (1) was more involved, and gave consistently high results when compared with the gravimetrically determined total sulfur.

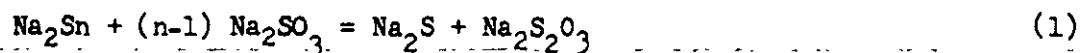
INTRODUCTION

As a result of experimental work conducted by the Institute Pulping laboratory, an increase in pulp yield was realized, using sulfide-soda cooking liquor rich in polysulfide. However, the cooking liquor prepared by dissolving sulfur in NaOH presented two major problems; first, a large excess of thio-sulfate was formed which is inactive in the cooking process; second, a reliable analytical scheme for analysis of the liquor was needed.

This project was initiated with a two-fold objective:

- (1) To minimize the formation of $\text{Na}_2\text{S}_2\text{O}_3$, and
- (2) To develop a reliable scheme of analysis and to investigate Berthier's (1) and Kesler and Han's (2) work on polysulfide sulfur analysis.

Berthier's (1) method for polysulfide analysis is based on the reaction:

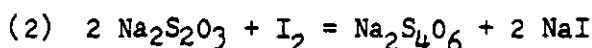
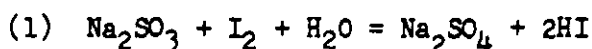


where an excess of Na_2SO_3 is added to the liquor at 50°C. The sulfide is precipitated out with zinc sulfate and sodium carbonate. The resulting liquor is iodometrically titrated according to standard TAPPI methods, using formaldehyde to inactivate the sulfite in the second titration. This value for thiosulfate is subtracted from the value of the original thiosulfate present in the liquor, thus giving the Na_2Sn .

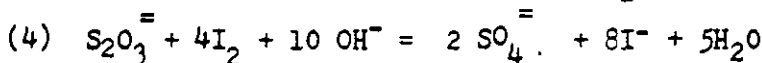
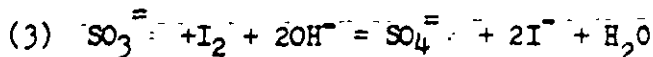
According to Kesler (2), the TAPPI method gave erratic results, partly due to the difficulty in judging the starch endpoint in the presence

of formaldehyde, and partly due to the reason discovered by Haegland and Loschbrandt (3). Therefore, after the sulfite treatment and sulfide precipitation, as described by Berthier, the liquor was titrated according to the method of Kesler and Han for the thiosulfate and sulfite content. This method is a part of the over-all analysis scheme proposed by Kesler and Han, which eliminates the use of formaldehyde in distinguishing between sodium thiosulfate and sodium sulfite.

Their determination of sodium thiosulfate in the presence of sodium sulfite is based on two titrations, one in strongly acid medium and one in strongly alkaline medium. Sulfite and thiosulfate react with acidic iodine according to the following reactions:



In alkaline medium they react according to the following reactions:



If: $x = \text{Na}_2\text{SO}_3$ g. mole/l.

$y = \text{Na}_2\text{S}_2\text{O}_3$ g. mole/l.

A = titration in acidic medium, eq./l.

B = titration in alkaline medium, eq./l.,

then: $8y + 2x = B$

$$\underline{y + 2x = A}$$

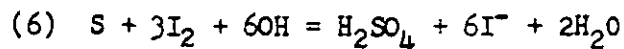
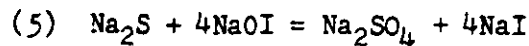
$$7y = B-A, \quad \text{or } y = \frac{B-A}{7}$$

~~Kesler and Han's method of analysis for polysulfide is based on the~~
following reactions and titrations.

Titration 1 (TRC-B)

Liquor is titrated with standard iodine in alkaline medium which is a measure of the sulfide, sulfite, thiosulfate, and polysulfide.

The reactions for sulfide and polysulfide are as follows:

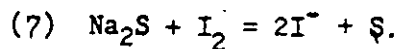


The reactions for sulfite and thiosulfate are given in the previous paragraph as Reactions (3) and (4).

Three additional titrations are required to determine the actual amount of sulfide, sulfite, and thiosulfate, the difference between TRC-B and these amounts being the polysulfide sulfur.

Titration 2 (TRC-A)

This titration is carried out in acid medium, and is a measure of sulfide according to the following reaction:



The reactions for sulfite and thiosulfate are given in Reactions (1) and (2), respectively, while polysulfide does not react.

Titration 3 (SFRC-A)

Titration 3 is carried out in acid medium on the liquor from which the sulfide and polysulfide have been removed, and is a measure of sulfite and thiosulfate according to reactions (1) and (2), respectively.

Titration 4 (SFRC-B)

Titration 4 is carried out in alkaline medium on the liquor from which the sulfide and polysulfide have been removed, and is a measure of sulfide and polysulfide according to Reactions (3) and (4), respectively.

The concentrations of the individual constituents in gram-moles per liter are calculated from the analytical results in gram-equivalents/liter as follows:

$$\text{Na}_2\text{S}_2\text{O}_3 = \frac{(\text{SFRC-B}) - (\text{SFRC-A})}{7}$$

$$\text{Na}_2\text{SO}_3 = \frac{(\text{SFRC-A}) - (\text{Na}_2\text{S}_2\text{O}_3)}{2}$$

$$\text{"Poly" S} = \frac{\text{TRC-B} - (8 \text{ Na}_2\text{S} + 8 \text{ Na}_2\text{S}_2\text{O}_3 + 2 \text{ Na}_2\text{SO}_3)}{6}$$

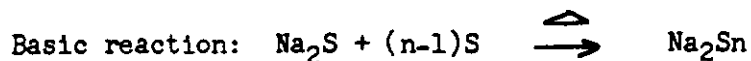
Complete procedures for the Berthier proposal and the Kesler and Han proposal may be found in Appendices I and II.

EXPERIMENTAL

The general plan called for the preparation of polysulfide cooking liquors to be made under various conditions. In conjunction with this, a complete analysis was carried out for Na_2S , Na_2Sn , Na_2SO_3 , and $\text{Na}_2\text{S}_2\text{O}_3$ according to the method of Kesler and Han.⁽²⁾ In addition, polysulfide was determined according to Berthier's method (1). A BaSO_4 total sulfur analysis was run on each liquor to check the volumetric results.

A brief description of each liquor as to components and conditions follows, with analytical results given in Table I.

Liquor No. 1



137.8 g. $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ was dissolved in 750 ml. H_2O at 85°C . 18.4 g. sulfur, to give a total of 36 g./l. S, was added to a 2-l. beaker with stirring. The solution was heated to 85°C . because of difficulty in dissolving the sulfur. A mechanical beater would have facilitated wetting the sulfur. When all of the sulfur was dissolved, the solution was cooled to room temperature and 255 grams of NaOH was added. At this point the volume was checked and found to be over one liter. Therefore, less H_2O should have been used to dissolve the $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$. The system was open to the air at all times, heated and stirred on a Waco Agit-Thermo Magic Stir.

Liquor No. 2

The liquor was made up as a duplicate of Liquor No. 1. However, this liquor was diluted to exactly one liter.

Liquor No. 3



300 grams of NaOH were dissolved in H₂O and 36 grams of sulfur added. It was necessary to heat to 70°C. and agitate the solution for three hours to dissolve the sulfur. The system was open to the air.

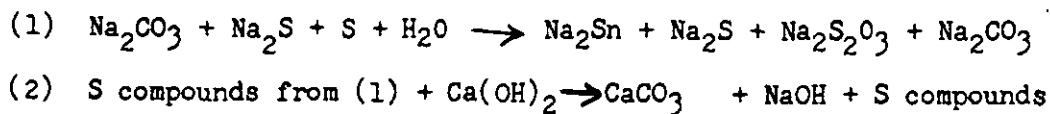
Liquor No. 4

Basic reaction: Same as Liquor 3, plus atmosphere of nitrogen.

Distilled H₂O was deaerated on the Institute vacuum for 3 hours. 36 grams of sulfur plus 300-ml. of deaerated H₂O were placed in the reaction jar (see Figure 1). The jar was evacuated to a 3rd mercury pressure and pressurized to 3rd of mercury with nitrogen, the nitrogen being bubbled through the stirring H₂O and sulfur. This procedure was repeated 5 times. Nitrogen gas was then bubbled through the solution for 5 minutes, the nitrogen pressure being in equilibrium with the vacuum. Pressure changes were controlled with a manometer. 300 grams of NaOH were dissolved in 400-ml. of deaerated H₂O with minimum stirring and added to the reaction jar. Nitrogen was again bubbled through the stirring solution for 5 minutes and at frequent intervals during the 2-hour dissolving time. The solution was heated to 85°C. and held at atmospheric pressure under nitrogen during the entire reaction period.

Liquor No. 5

Basic reaction:



343.1 g. Na₂CO₃ was added to 650-ml. H₂O. 123.07-g. Na₂S.9H₂O was

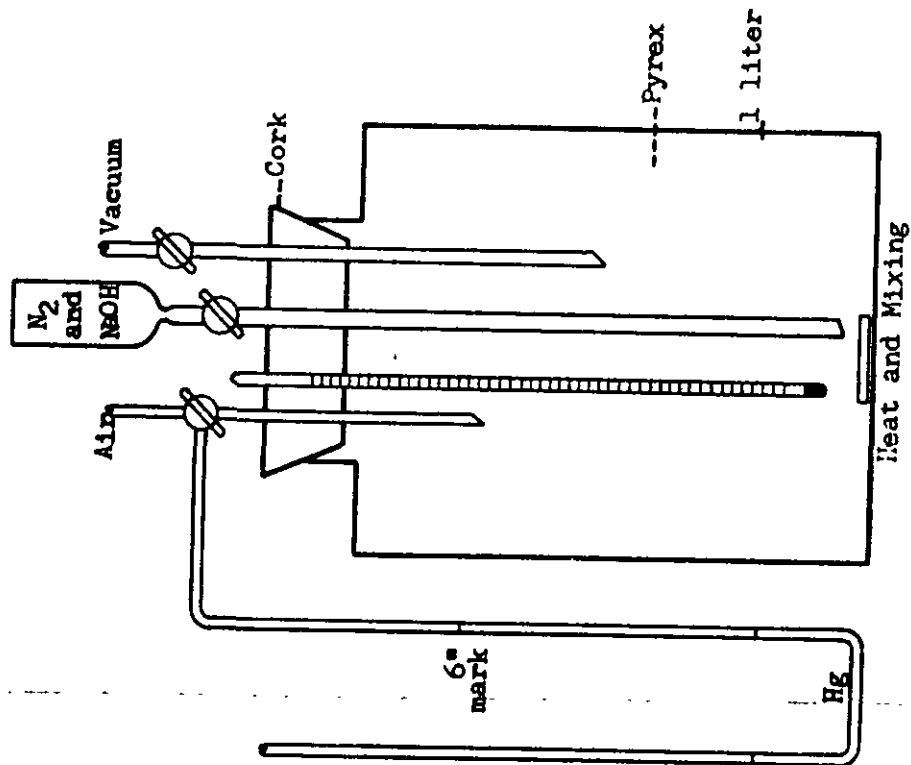


Figure 1. Reaction Jar

dissolved in 100-ml. H_2O ; this solution plus 19.6-g. of sulfur (giving a sulfur total of 36 g./l.) were added to the Na_2CO_3 solution. The entire system was heated to $60^\circ C$. and stirred for two hours. 240.1-g. $Ca(OH)_2$ was suspended in approximately 200-ml. H_2O and added to the Na_2CO_3 , $Na_2S \cdot 9H_2O$, S system. This mixture was stirred for 3 hours. The volume of the mixture was approximately 1.300 liters and open to the air at all times.

Liquor No. 6

Basic reaction: Same as for Liquor 5.

This liquor was a duplicate of Liquor 5 except for a few changes in conditions and amount of H_2O used. According to the Rubber Publishing Co. handbook, the optimum temperature for dissolving Na_2CO_3 is $30^\circ C$. at a rate of 50.5-g./100 ml. Therefore, the theoretical H_2O needed and used was 679.4 ml. The Na_2CO_3 solution was heated to $30^\circ C$. and stirred until all Na_2CO_3 was dissolved before adding the Na_2S which had been first dissolved in a minimum amount of H_2O . The sulfur was added and the mixture stirred and heated until it was dissolved. The $Ca(OH)_2$ was not suspended in H_2O , but rather was added directly as a powder. This mixture was stirred for 3 hours. The volume was approximately 1 liter. The system was open to the air at all times.

TABLE I
ANALYSIS OF POLYSULFIDE COOKING LIQUORS

Liquor Identification	Sulfur Added, g./h.	Thiosulfate (as S), g./h.	Sodium Sulfide (as S), g./h.	Polysulfide (as S) ¹ , g./h.	Polysulfide (as S) ² , g./h.	Total Sulfur ¹ , g./h.	Total Sulfur ² , g./h.	Total Thiosulfate ¹ , g./h.	Sulfide ¹ , g./h.	Polysulfide, g./h.	Total Alkali, eq./h.	Active Alkali, eq./h.
Liquor No. 1 10.4 g. S dissolved in 137.84 g. Na ₂ S ₂ O ₄ + 255 g. NaOH diluted to approximately 1 liter and in air	36	4.2	16.3	13.1	14.5	33.6	35.0	33.19	48.5	39.0	--	--
Liquor No. 2 Percent same as liquor No. 1; diluted to 1 liter in air.	36	4.29	18.82	13.28	16.4	36.4	39.52	36.75	51.7	36.5	--	--
Liquor No. 3 200-g. NaOH + 36 g. S diluted to 1 liter in air	36	8.72	11.33	14.29	16.61	34.34	36.66	34.7	33.0	41.6	--	--
Liquor No. 4 300-g. NaOH + 36-g. S diluted to 1 liter. Closed system under nitrogen.	36	11.94	12.01	10.07	13.28	34.02	37.29	35.37	35.3	29.6	--	--
Liquor No. 5 34.3-g. Na ₂ CO ₃ + 123.07-g. Na ₂ S ₂ O ₄ + 19.6-g. S (Ca(OH) ₂ 240.1 g. diluted to approximately 1 liter.	36	7.00	12.99	13.58	13.84	33.21	34.25	33.65	37.9	40.99	3.91	3.44
Liquor No. 6 Content same as liquor No. 5 diluted to 1 liter.	36	5.28	13.57	16.18	18.02	35.03	36.92	35.0	38.7	46.2	4.41	3.89
Spring 1957 S + NaOH	--	--	--	--	--	--	--	--	31.8	33.72	--	--
Earthier, S + NaOH Liquor No. 1	--	--	--	--	--	--	--	--	21.8	43.8	--	--
Liquor No. 2	--	--	--	--	--	--	--	--	28.7	43.13	--	--
Liquor No. 3	--	--	--	--	--	--	--	--	29.0	42.73	--	--

¹Progress Report Mine, Project 1568.
²Assoc. Technique de l'Industrie Papetière, Bull. No. 4:93-106(1953).
³Gravimetric determination, barium sulfate.

DISCUSSION OF RESULTS

I. MINIMIZE FORMATION OF THIOSULFATE

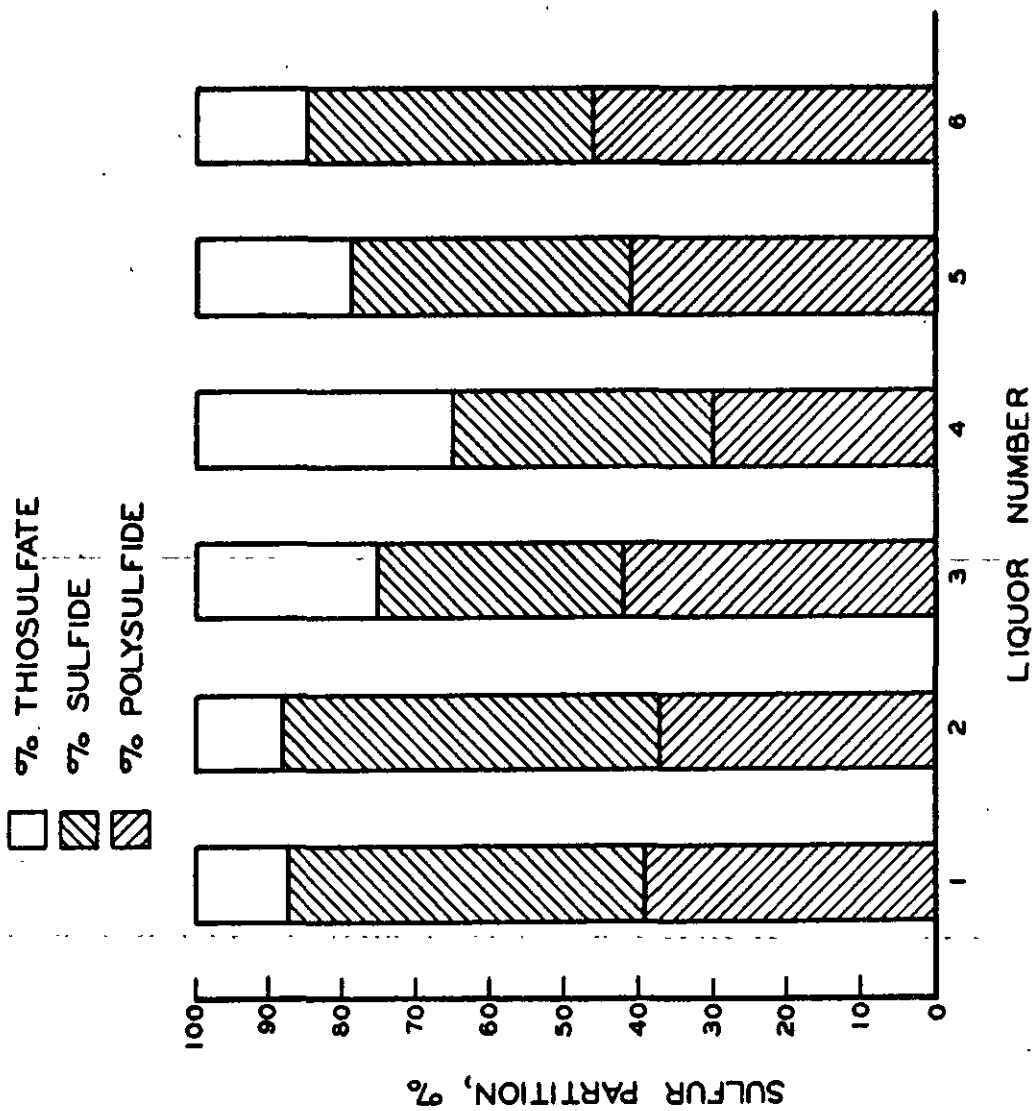
Results indicate the most desirable method of liquor preparation is adding elemental sulfur to a solution of sodium sulfide, as with Liquors No. 1 and 2, allowing this reaction to come to equilibrium--i.e., $\text{Na}_2\text{S} + \text{S} \rightleftharpoons \text{Na}_2\text{S}_2$, before adding the sodium hydroxide. This gives the least amount of thiosulfate while at the same time a high content of polysulfides. Liquor No. 3 (adding elemental sulfur to a solution of sodium hydroxide) indicates the presence of NaOH facilitates the formation of thiosulfate. The desirability of the methods of Liquors No. 1 and 2 is offset to some extent by the need for a modified recovery system which would separate the sodium carbonate and sulfur compounds in the green liquor.

The recovery problem led to the investigation of a sodium carbonate plus sodium sulfide plus elemental sulfur system due to the belief the presence of sodium hydroxide facilitates the formation of thiosulfate. That is, do not causticize until after elemental sulfur has been added to the purified green liquor. This scheme would fit the present recovery systems. This proved quite successful. Although the thiosulfate was 3% higher than the sodium sulfide plus sulfur system (Liquors No. 1 and 2), it was in turn 10% lower than the usual sodium hydroxide plus sulfur systems (Liquor No. 3). Liquor No. 6 was used for these comparisons as it was prepared under more desirable conditions than Liquor No. 5.

Liquor No. 4 was prepared in a closed system under nitrogen. The water used was deaerated and stripped of oxygen by bubbling nitrogen through it.

Figure 2

Liquor Components



The nitrogen atmosphere did not succeed in minimizing thiosulfate as the results clearly show. Therefore, we may conclude the formation of thio-sulfate is an internal reaction facilitated by the presence of NaOH. (Fig. 2).

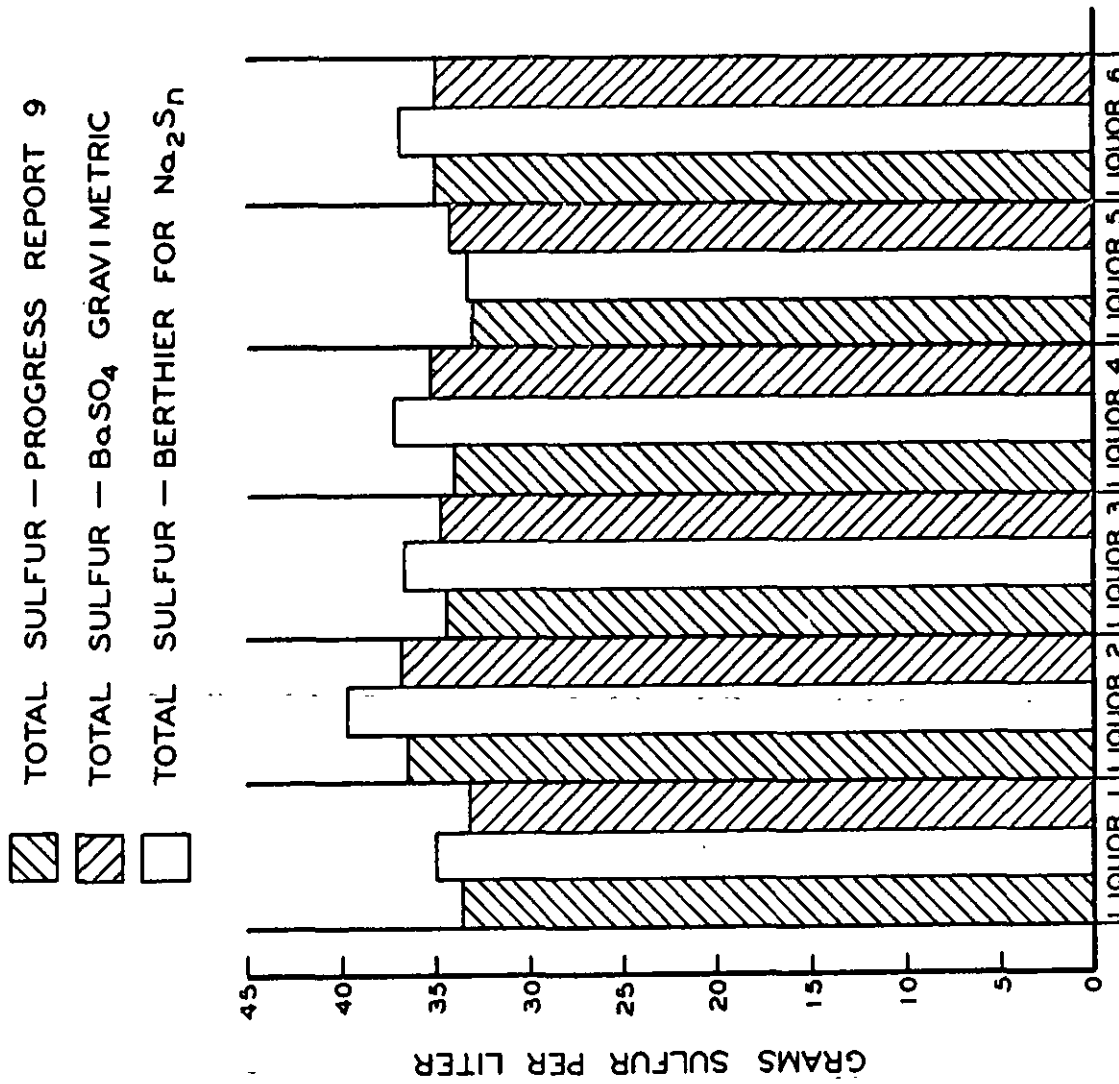
II. COMPARISON OF THE KESLER-HAN AND BERTHIER ANALYSES FOR POLYSULFIDES

Comparison of the volumetric total sulfur per liter to the gravimetric total sulfur points out a much closer agreement between the Kesler and Han method and the gravimetric results than between the Berthier method and the gravimetric results. The Kesler and Han results are consistently a bit lower but to such a small degree as to be almost insignificant. Another advantage of the Kesler and Han method is the time involved; only one additional titration is needed, while the Berthier method involves the sulfite treatment, the sulfide precipitation, and two titrations. Another disadvantage of the Berthier method is the consistently higher results. This may be explained as being due to the nature of the reaction. The reaction

$(n-1)\text{Na}_2\text{SO}_3 + \text{Na}_2\text{S} \rightleftharpoons \text{Na}_2\text{S} + \text{Na}_2\text{S}_2\text{O}_3$ is driven to the right by the excess sodium sulfite added. However, because the liquor itself contains Na_2S and $\text{Na}_2\text{S}_2\text{O}_3$, more polysulfide may be formed by a reversible reaction, thus giving a higher polysulfide content. (Fig. 3).

Figure 3

Comparison of Total Sulfur Data



CONCLUSIONS

(1) The most desirable method of preparing a polysulfide-rich cooking liquor is to dissolve elemental sulfur in a solution of sodium sulfide, then add NaOH.

(2) The most advantageous method from a commercial standpoint is to dissolve elemental sulfur in a solution of sodium carbonate and sodium sulfide, then causticize.

(3) An atmosphere of nitrogen was no detriment to the formation of thiosulfate.

(4) The Kesler and Han analysis scheme proved to be superior both in accuracy and time involved for this particular purpose.

LITERATURE CITED

- (1) Assoc. Technique de l'Industrie Papetiere, Bull. No. 4:93-106(1953).
- (2) Tappi 40, no. 10:802-809(Oct., 1957).
- (3) Haegland, B., and Loschbrandt, F. Norsk. Skogind. 9, no. 5:172-76(1955).
- (4) Progress Report Nine, Project 1568.

APPENDIX I

Method of Analysis for Polysulfide--Rene Berthier (1)¹

Sn-1 from Polysulfides

The basic reaction is $\text{Na}_2\text{Sn} + (n-1) \text{Na}_2\text{SO}_3 = \text{Na}_2\text{S} + (n-1) \text{Na}_2\text{S}_2\text{O}_3$.

To a 50-ml. sample of the original liquor, an excess of 0.4 N Na_2SO_3 (250) is added and heated on a steam bath at 50°C. for 15 minutes or until the yellow color disappears. Transfer the treated sample to a 250-ml. volumetric flask and add a 30-ml. 1M Zn sulfate -30 ml. 1MNa carbonate suspension to remove sulfide; dilute to volume. Test the supernatant liquid for complete sulfide precipitation with ammoniacal silver nitrate.

(a)¹ Filter through quantitative filter paper such as Whatman No.42 in a Büchner funnel using mild suction. It may be necessary to pass the first filtrate through the pad again to obtain a clear filtrate. Measure 20-30-ml. standard iodine into a 250-ml. Erlenmeyer flask and add 10-ml. 2N sulfuric acid. Pipet 10-or 25-ml. of clear filtrate into the acidified iodine while swirling the contents of the flask and titrate the excess iodine with standard sodium thiosulfate. Record the results in equivalents/liter. Duplicate titrations should agree within 4×10^{-3} equivalents/liter.

(b) Add 20-ml. of 12N sodium hydroxide solution to a 250-ml. ground glass stoppered Erlenmeyer flask and pipet in 10 or 25-ml. of the clear filtrate. Titrate with 20-25 ml. of standard iodine solution. Cool the flask in an ice water bath, dilute 20-40 ml. and add 21-22 ml. of concentrated (12N) hydrochloric acid, re-cool to room temperature, and titrate the liberated iodine with standard 0.1 N sodium thiosulfate. Record the results in equivalents/liter.

¹Method modified according to Kesler and Han (4); also see pp. 3,4 of this report for explanation.

Calculate the thiosulfate; from this value subtract the value of the original thiosulfate present. The difference is polysulfide (Sn-1) in g.atoms/l.

APPENDIX II

Method for Analysis as Applied to Polysulfide Cooking Liquors

Kesler, R. B., and Han, S. T. (2,4)

Total Sulfur

Dilute 10-ml. of the liquor to 100-ml. in a volumetric flask. Pipet 25-ml. of the diluted liquor into a 250-ml. beaker and add 10-ml. 2N sodium hydroxide and 25-ml. of water. Add 25-ml. 30% hydrogen peroxide and cover the beaker with a watch glass. If the solution foams and heats excessively, immerse it in a container of water. Let it stand about 12 hours or overnight. Bring it to a boil by heating gradually, and boil for a few minutes. Cool and add 1 drop of methyl orange. If the color fades, hydrogen peroxide is still present and more boiling is required. When all the excess hydrogen peroxide has been destroyed by boiling, bring the solution to neutrality with 1N HCl and methyl orange. Adjust the volume so that the beaker is slightly more than half full, add 5-ml. of concentrated hydrochloric acid. In a 150-ml. beaker place 25-ml. of 10% barium chloride solution and 50-ml. water. Bring the contents of both beakers to the boiling point and rapidly pour the hot barium chloride solution into the 250-ml. beaker, while vigorously stirring the contents of the 250-ml. beaker. Continue stirring for a few minutes and let the beaker stand in a warm place for about an hour. Following standard

gravimetric procedure, filter, ignite, and weigh the barium sulfate.

TRC-A

In a volumetric flask, dilute 10-ml. of the green liquor to 100-ml. with distilled water. From a buret, measure 35-45-ml. standard 0.2N iodine into a 250-ml. Erlenmeyer flask. Add 10-ml. of 2N sulfuric acid and pipet 10 or 25-ml. dilute liquor into the iodine while swirling or mixing vigorously the contents of the flask. Titrate the excess iodine with standard sodium thiosulfate to the starch endpoint. Record the results in equivalents/liter. Duplicate titrations should agree within 4×10^{-3} equivalents/liter.

TRC-B

To a 250-ml. flask add 30-ml. 12N NaOH solution. Dilute 10-ml. of the liquor to 100-ml. Pipet 10-ml. of the diluted liquor into the flask. Start mixing at a slow speed (the contents of the flask will now assume a yellow tinge), and begin adding iodine at a steady drop-wise rate. As more iodine is added and the volume increases, the speed of the mixer should be increased. As the endpoint approaches, the solution will lose its yellow color and turn colorless and clear. At the endpoint, a yellow color will again appear and increase in intensity as more iodine is added. At the endpoint (reappearance of yellow color), note the approximate volume of iodine added, and continue adding iodine until at least 15-ml. in excess of the endpoint have been added. Let the mixture stand for a minute or two and dilute the contents of the flask to about 125-ml. with distilled water. Mix thoroughly and cool in an ice-water bath. While mixing, add 35-ml. concentrated HCl, cool. Titrate the liberated

iodine with standard sodium thiosulfate. Record the results in equivalents per liter. Duplicate titrations should agree within 5×10^{-3} equivalents per liter.

SFRC-A

Before proceeding with the actual determination of SFRC, a preliminary test must be made on the liquor to determine how much of the sulfide-precipitating agent must be added to an aliquot of the liquor to quantitatively remove all the sulfide (and polysulfide). This is done as follows.

Pipet 50-ml. of the liquor into a 150-ml. beaker. Add a freshly prepared suspension of zinc carbonate made by mixing together 20-ml. each of 1M zinc sulfate and 1M sodium carbonate. Mix thoroughly and let the mixture stand until there is about 1/2" of clear liquor over the settled precipitate. Test for complete sulfide precipitation by adding 1 drop of ammoniacal silver nitrate to the clear liquor. If a black or brown cloud or curd forms immediately in the clear liquor, more zinc carbonate suspension must be added. Prepare more zinc carbonate suspension by mixing 5-ml. each of the sodium carbonate and zinc sulfate solutions. Add this to the liquor and mix thoroughly. Let the solids settle, and test the clear liquor again with ammoniacal silver nitrate. Repeat the addition of zinc carbonate suspension until a test with ammoniacal silver nitrate indicates the absence of sulfide ions in the supernatant liquid. Note the sums of the respective volumes of sodium carbonate and zinc sulfate used and discard the tested mixture.

Pipet 50-ml. of the liquor into a 250-ml. volumetric flask, and add the amount of zinc carbonate suspension necessary for complete sulfide precipitation as determined in the preliminary test. Mix thoroughly and

dilute to the mark with freshly boiled distilled water. Do not add caustic or oxidation inhibitors.

Filter through quantitative filter paper, such as Whatman No. 42, in a Büchner funnel using mild suction. It may be necessary to pass the first filtrate through the pad again to obtain a clear filtrate. Measure 20-30-ml. standard iodine into a 250-ml. Erlenmeyer flask and add 10-ml. 2N sulfuric acid. Pipet 10- or 25-ml. of clear filtrate into the acidified iodine while swirling the contents of the flask and titrate the excess iodine with standard sodium thiosulfate. Record the results in equivalents/liter. Duplicate titrations should agree within 4×10^{-3} equivalents/liter.

SFRC-B

Add 30-ml. 12N NaOH to a 250-ml. flask, and pipet in 10-ml. of the clear filtrate obtained in SFRC-A. Add 25-35-ml. standard iodine in a rapid drop-wise manner while swirling the contents of the flask. Cool and add 35-ml. concentrated HCl in the manner described in TRC-B. Titrate the liberated iodine with standard sodium thiosulfate and report the results in equivalents/liter. Duplicate titrations should agree within 5×10^{-3} equivalents/liter.

Calculations:

$$\text{Na}_2\text{S}_2\text{O}_3 = \frac{(\text{SFRC-B}) - (\text{SFRC-A})}{7}$$

$$\text{Na}_2\text{SO}_3 = \frac{(\text{SFRC-A}) - (8\text{Na}_2\text{S}_2\text{O}_3)}{2}$$

$$\text{Na}_2\text{S} = \frac{(\text{TRCA}) - (\text{SFRC-A})}{2}$$

$$\text{"poly" S} = \frac{(\text{TRCB}) - (8\text{Na}_2\text{S} + 8\text{Na}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{SO}_3)}{6}$$

$$\text{Total sulfur, g./l.} = \frac{\text{g. BaSO}_4 \times 0.1374 \times 1000}{\text{ml. liquor}}$$

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BEATER EVALUATION OF SAMPLES OF KRAFT PULP COMMERCIALY PRODUCED BY A CONTINUOUS PROCESS

SUMMARY

A Canadian softwood kraft pulp, produced by a continuous process, has recently been put on the market. Samples of the unbleached and bleached pulps which had never been dried and a sample of the bleached dry lap pulp were presented for evaluation. For comparison with the latter pulp, strength data for a commercial bleached Southern pine and a bleached Douglas-fir kraft dry lap pulp, available from another project, were included in this report.

Conventional evaluations were performed in a 1.5-lb. Valley beater. The strength properties of the several pulps were compared at two freeness levels. In addition, the properties were considered graphically in several ways and certain conclusions were drawn from the data.

The Canadian (St. Regis) pulp is made from a mixture of equal parts of black spruce and lodgepole pine. It appears to have a very high potential for developing fiber-to-fiber bonding--especially in the undried form, and to have very good intrinsic fiber strength. Drying the pulp seems to result in some loss of both properties. The pulps were all high in bursting strength, tensile strength, and folding endurance and were low in tearing strength, when compared at similar beating times or freeness levels.

When the properties of the St. Regis dry lap were compared with those of the other two commercial dry lap pulps, it was seen to be higher in bursting strength, tensile strength, and folding endurance. The pine and especially the Douglas-fir pulp were higher in tearing resistance. Fiber strength was highest for the St. Regis pulp and lowest in the case of the pine pulp.

It was deduced that the high degree of bonding achieved by the St. Regis pulp contributed to its outstanding bursting and tensile strength properties and to its poor tear resistance by causing fiber rupture in preference to bonding failure in the tear test. The reverse was true of the Douglas-fir and Southern pine pulps. The Douglas-fir pulp, especially, showed lack of bonding potential in its low burst, tensile, and folding strengths and very high tear values. Differences in intrinsic fiber strength seemed to play a minor role in the handsheet strength properties, probably because the differences involved were not as outstanding as were the fiber length and fiber-to-fiber bonding differences.

INTRODUCTION

The St. Regis Paper Company has recently put on the market a kraft pulp manufactured in a newly constructed plant in Hinton, Alberta, Canada. This fiber, which is the first of the type to be produced on this continent in a continuous pulping system, is said to have properties different from those of any other commercial pulp.

The Institute has obtained samples of unbleached and bleached slush stock, as well as a sample of the finished product, which is a dry lap bearing the brand name "Hi-Brite," for the purpose of applying some of the usual tests for physical characteristics.

EXPERIMENTAL

The three pulp samples were given identical treatment in a calibrated 1.5-lb. Valley beater using TAPPI Method T 200-m-45, modified to the extent that the interval samples were not cleared in a TAPPI disintegrator prior to formation of the handsheets. The handsheet formation and testing methods used are covered in TAPPI Methods T 205 m-53 and T 220 m-53, and the freeness tests are described in Method T 227 m-50. The two slush samples were carefully dewatered on a filter paper in a table Büchner funnel prior to charging to the beater, and the dry lap pulp was soaked overnight in filtered tap water and defibered under a Williams stirrer equipped with a TAPPI disk.

The results of the freeness tests and the handsheet evaluations are shown in Table I, along with similar results obtained for a bleached Southern

pine dry lap and a bleached Douglas-fir dry lap kraft pulp.

DISCUSSION OF RESULTS

An article (1) in the Pulp and Paper Magazine of Canada states that the mill at Hinton is pulping a mixture of equal parts of black spruce and lodgepole pine. Such a mixture of woods is probably unique to this particular mill, and therefore it is difficult to assess which qualities inherent in the pulp stem from the fiber source and which from the cooking process.

In order to make comparisons among the three Hinton pulps, we must assume that the samples were carefully chosen so that they are all representative of the same batch of pulp. If this is not so (and some of the test results indicate that batch differences may exist), then these particular comparisons must be used with caution. The comparisons among the three dry lap pulps may be used with more assurance, remembering only that we are speaking of single samples of each of these broad classifications of wood sources.

The physical properties data shown in Table I were plotted against beating time in Figures A through E in the appendix. From these graphs, the properties at two freeness levels were determined and arranged in Table II. Reference to the data in this form gives some insight into the character of the several pulps. The unbleached Pulp B, which had never been dried, was slow to respond to the beating process. It displayed excellence in those properties which rely on fiber-to-fiber bonding (bursting and tensile strengths and folding endurance), and was apparently not outstanding in tearing strength. Since the zero-span tensile strength was very good, it appears that the intrinsic fiber strength is also favorable. Bleached slush Pulp A, which also

TABLE I
 BEATER EVALUATION

		Unbleached Slush Pulp B	Bleached Slush Pulp A	Bleached Dry Lap C	Riegel Dry Lap	Harmac Dry Lap
Canadian Standard freeness, cc.	0 ¹	735	700	650	730	750
	5	690	690	650	720	720
	15	670	635	605	680	680
	30	640	545	535	550	570
	50	570	415	425	365	420
	70	465	260	305	205	210
Apparent density (airdry basis weight, lb./ caliper, mils)	0	10.0	11.6	10.8	10.6	8.7
	5	11.2	13.0	11.8	11.2	9.6
	15	12.5	14.0	13.3	12.2	10.9
	30	13.5	15.1	14.1	12.9	11.8
	50	14.3	15.3	14.5	13.2	12.4
	70	14.7	16.0	15.1	14.0	13.2
Bursting strength, pt./100 lb. airdry basis weight	0	52	63	46	35	15
	5	88	106	75	61	33
	15	123	143	125	90	65
	30	153	157	157	116	110
	50	167	172	174	123	130
	70	174	185	169	135	139
Tear factor, tearing strength of 16 sheets/airdry basis weight	0	2.36	2.64	3.06	3.17	2.27
	5	1.62	1.58	2.27	2.87	3.48
	15	1.30	1.19	1.46	2.06	3.81
	30	1.09	0.99	1.23	1.64	2.36
	50	1.00	0.91	1.14	1.54	1.93
	70	0.96	0.86	0.99	1.41	1.74
Tensile strength (corrected to a 45-lb. basis wt. sheet), lb./in.	0	15.0	16.1	13.4	10.4	6.0
	5	21.9	24.3	20.1	15.1	10.2
	15	30.5	33.2	28.5	21.3	16.2
	30	35.5	36.9	35.2	24.9	23.9
	50	39.4	39.0	37.3	29.1	27.0
	70	41.2	41.6	40.5	29.9	29.7
Zero-span tensile strength, lb./in.	0	41.8	40.2	45.7	38.3	41.7
	5	47.0	45.4	47.3	40.5	40.5
	15	48.4	49.9	48.4	40.1	46.3
	30	50.0	54.2	51.6	45.5	48.3
	50	51.2	56.8	50.7	46.2	50.3
	70	52.2	54.4	54.5	48.6	46.3
M.I.T. fold	0	49	73	26	12	2
	5	464	528	179	63	13
	15	962	1259	752	390	155
	30	1388	1643	1188	796	753
	50	1091	2243	1619	1011	1015
	70	1848	2472	1799	1439	1753

¹Beating time, min.

TABLE II

COMPARISON OF PULP PROPERTIES AT TWO FREENESS LEVELS

	Unbleached Slush Pulp B	Bleached Slush Pulp A	Bleached Dry Lap C	Bleached Riegel Dry Lap	Bleached Harmac Dry Lap
<u>Comparison at 600-cc. Canadian Standard Freeness</u>					
Beating time, min.	40.5	22.5	16.5	24.0	26.0
Apparent density (airdry basis weight, lb./ caliper, mils)	13.9	14.8	13.3	12.7	11.6
Bursting strength, pt./100 lb. airdry basis weight	162	158	127	105	99
Tear factor, tearing strength of 16 sheets/airdry basis weight	1.06	1.07	1.41	1.72	2.66
Tensile strength (corrected to a 45-lb. basis weight sheet), lb./in.	37.8	36.0	29.3	24.3	21.7
Zero-span tensile, lb./in.	56.5	53.2	49.6	45.2	47.5
Folding endurance, double folds	1750	1500	780	580	375

<u>Comparison at 400-cc. Canadian Standard Freeness</u>					
Beating time, min.	--	52.0	54.0	46.5	50.0
Apparent density (airdry basis weight, lb./ caliper, mils)	--	15.8	14.8	13.2	12.4
Bursting strength, pt./100 lb. airdry basis weight	--	178	174	124	130
Tear factor, tearing strength of 16 sheets/airdry basis weight	--	0.92	1.15	1.53	1.93
Tensile strength (corrected to a 45-lb. basis weight sheet), lb./in.	--	39.8	38.8	28.4	27.5
Zero-span tensile, lb./in.	--	56.5	52.5	46.4	50.1
Folding endurance, double folds	--	22.50	1590	1030	1125

had never been dried, had apparently suffered a minimum of degradation during the bleaching process, if the bleached pulp is truly representative of the unbleached after bleaching. Bursting and tensile strengths were only slightly under those which characterized the unbleached pulp, and tearing resistance was unchanged. Folding strength and zero-span tensile showed only a very little decrease after bleaching.

If the dry lap was actually from the identical batch from which the sample of bleached wet pulp was taken, then it seems apparent that the drying process to which the bleached Pulp C had been subjected had had a decided effect upon pulp quality. Sheet density was less at a given freeness than had been noted when the slush pulp was tested. Bursting and tensile strengths were slow to develop and did not reach the levels attained by the undried pulp. The folding endurance was only slightly more than half that of the undried pulp. Tearing strength improved, which would--when coupled with the other evidence--seem to indicate a lowering of the bonding potential. Lower zero-span tensile may reflect some damage to the fiber itself, imparted by the drying process.

When the bleached dry lap Pulp C is compared with two commercial dry lap pulps produced by the same pulping process in mills in widely separated parts of the continent, some interesting differences in physical properties are noted. In Table II it can be seen that the Riegel (Southern pine) and the Harmac (Douglas-fir) pulps did not match the pine-spruce pulp in properties which are thought to be dependent upon bonding potential (bursting and tensile strengths and folding endurance). Zero-span tensile strength was

also superior for the St. Regis pulps as compared to the Riegel and Harmac stocks. Only in tearing strength did the Douglas-fir and Southern pine pulps appear to excel. Even in this area, the Hinton pulp has certain advantages. Table III compares strength properties at a given level of tensile strength. Looking at the properties from this perspective might reasonably be suggested since it would not be necessary to refine a given pulp furnish beyond the degree which would achieve adequate bonding and formation characteristics. A level of 28 lb./in. tensile strength was chosen because it represents a point close to the maximum which can be attained by the comparison pulps. The St. Regis bleached pulp reached this level of strength in 15 minutes, while the Southern pine pulp needed 43 and the Douglas-fir pulp, 55 minutes to attain the same level. The Harmac pulp had tearing strength superior to the spruce-pine mixture even after this treatment, but the Southern pine tear was now comparable. What may be even more important, the Hinton pulp freeness at 28 lb./in. tensile was 610-cc. Canadian Standard, while the Southern pine and Douglas-fir pulps were reduced to 430 and 350-cc., respectively.

Figure 1 was made to show how the tearing strength varied with changes in tensile strength over the entire beating range. Reference to this graph shows that the Harmac pulp was superior in tearing strength at any level of tensile which it was able to achieve, but that all of the other pulps were essentially the same in this relationship.

Figure 2 shows how tensile strengths of the various pulps changed as drainage behavior was altered. In this respect, the dry lap St. Regis pulp was excelled only by the undried pulps. The Riegel was slightly higher over the entire beating range than the Harmac pulp.

TABLE III

COMPARISON OF PULP PROPERTIES AT A COMMON TENSILE STRENGTH

	Unbleached Slush Pulp B	Bleached Slush Pulp A	Bleached Dry Lap C	Riegel Bleached Dry Lap	Harmæ Bleached Dry Lap
Tensile strength (corrected to a 45-lb. basis weight sheet), lb./in.	28.0	28.0	28.0	28.0	28.0
Tear factor, tearing strength of 16 sheets/airdry basis weight	1.5	1.4	1.5	1.5	1.9
Bursting strength, pt./100 lb. airdry basis weight	108	120	123	122	132
Folding endurance, double folds	700	750	750	950	1300
Beating time, min.	10	8	15	43	55
Canadian Standard freeness, cc.	700	670	610	430	350

FIGURE 1

COMPARISON OF TEARING STRENGTHS AT SIMILAR LEVELS OF TENSILE STRENGTH

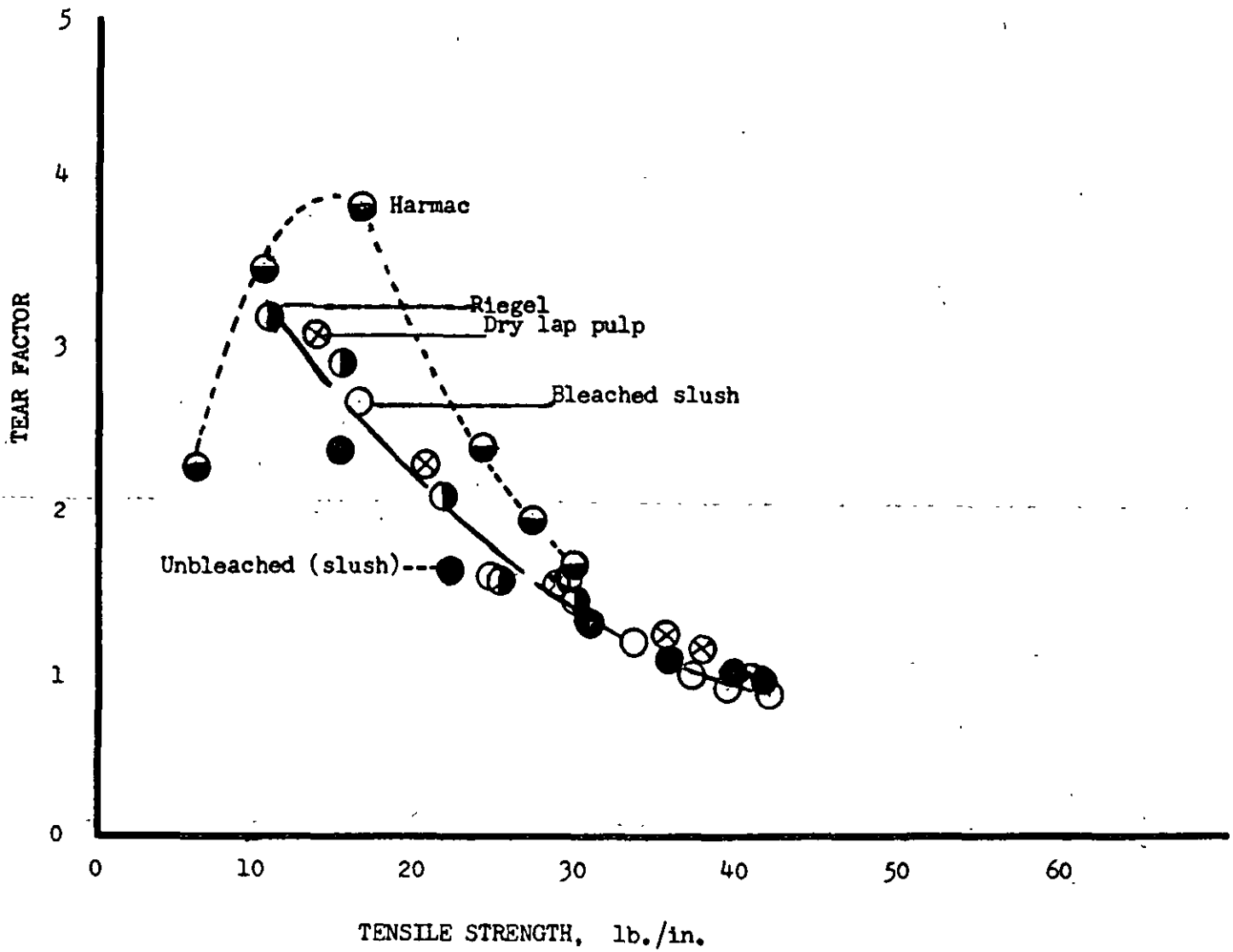
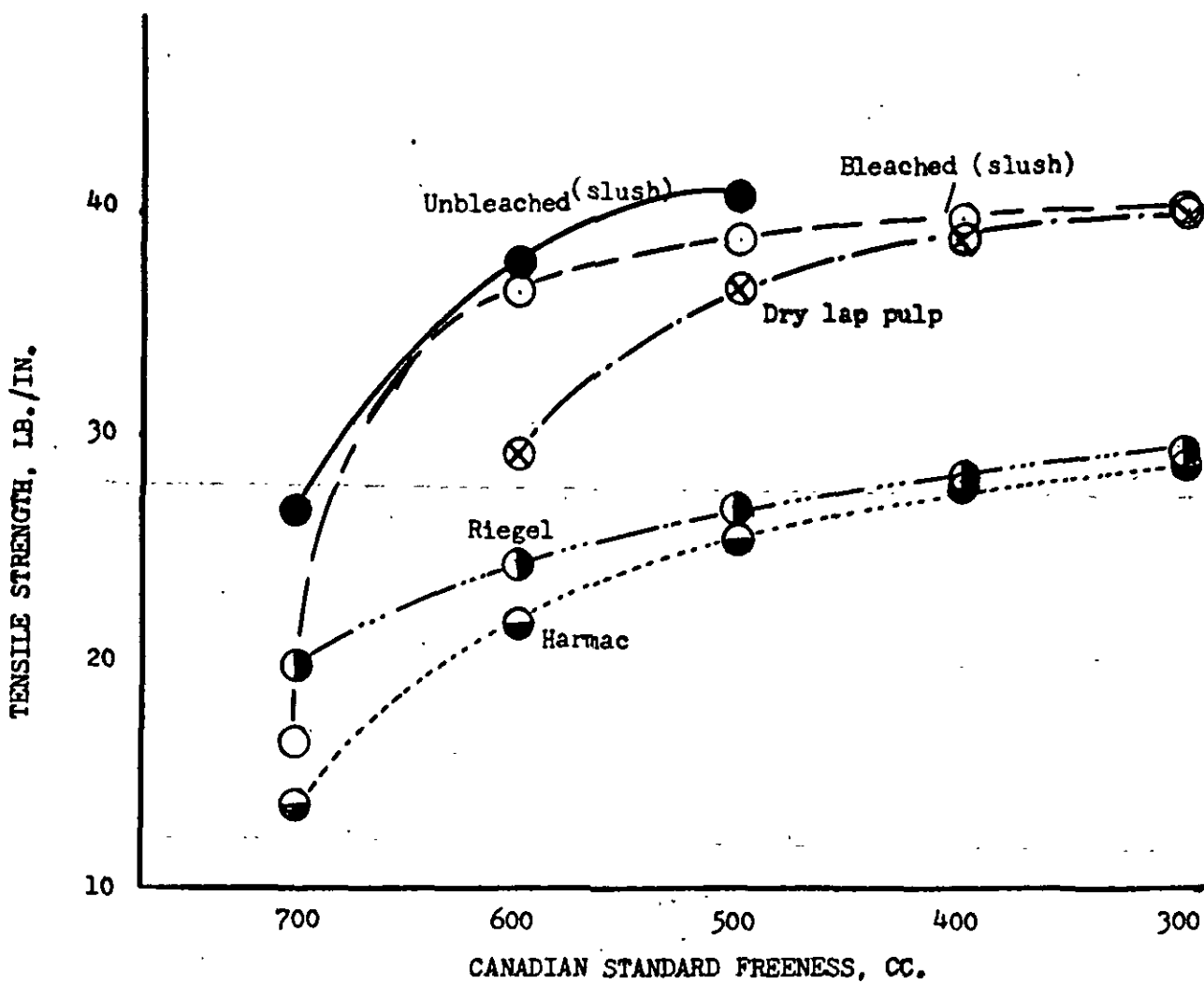


FIGURE 2
COMPARISON OF TENSILE STRENGTHS AT SIMILAR FREENESS LEVELS



One of the techniques used in this laboratory to estimate the bonding potential of a pulp (when direct measurements are lacking) is to calculate a value termed "degree of effective bonding," or DOEB. The reasoning behind this value and the method of calculation are included in the appendix. This was done at each of the several beating intervals and the results are shown in Table IV. In Figure 3 these values are plotted against freeness. When the pulps are compared in this manner, they rank in the same order shown in Figure 2, but the Riegel pulp shows slightly more advantage over the Harmac pulp than was apparent in the first figure.

In Figure 4, a value obtained by dividing tensile strength by DOEB is plotted against freeness. This ratio is used to cancel approximately the effect of bonding on the strength properties of the handsheets. When this is done, the Harmac pulp gives evidence of having some property or properties (other than bonding) which contribute to handsheet strength to a degree much in excess of that inherent in the other pulps.

The present state of our knowledge concerning pulp properties indicates that the properties other than bonding which contribute to sheet strength are fiber length, fiber strength, and sheet formation. Less is known about the effect of fiber wall thickness and fiber flexibility and extensibility, each of which may, however, have a considerable bearing on ultimate sheet strength. Of the above characteristics, we have measurement only of fiber strength, in this study, which is obtained by zero-span tensile tests. By dividing tensile strength by the product of DOEB and zero-span tensile and plotting these values against freeness, a ranking is obtained in which the contribution of bonding and fiber strength to tensile strength are approximately cancelled. This ratio is shown in

TABLE IV

DEGREE OF EFFECTIVE BONDING (DOEB)

Freeness Level (Canadian Standard Freeness, cc.)	Unbleached Slush Pulp B	Bleached Slush Pulp A	Bleached Dry Lap C	Riegel Bleached Dry Lap	Harmac Bleached Dry Lap
700	4.15	2.45	--	3.00	2.10
600	6.05	5.85	4.50	3.70	2.75
500	6.45	6.30	5.58	4.05	3.25
400	--	6.70	6.05	4.25	3.70
300	--	6.85	6.40	4.45	4.00

FIGURE 3
COMPARISON OF BONDING POTENTIALS AT SIMILAR FREENESS LEVELS

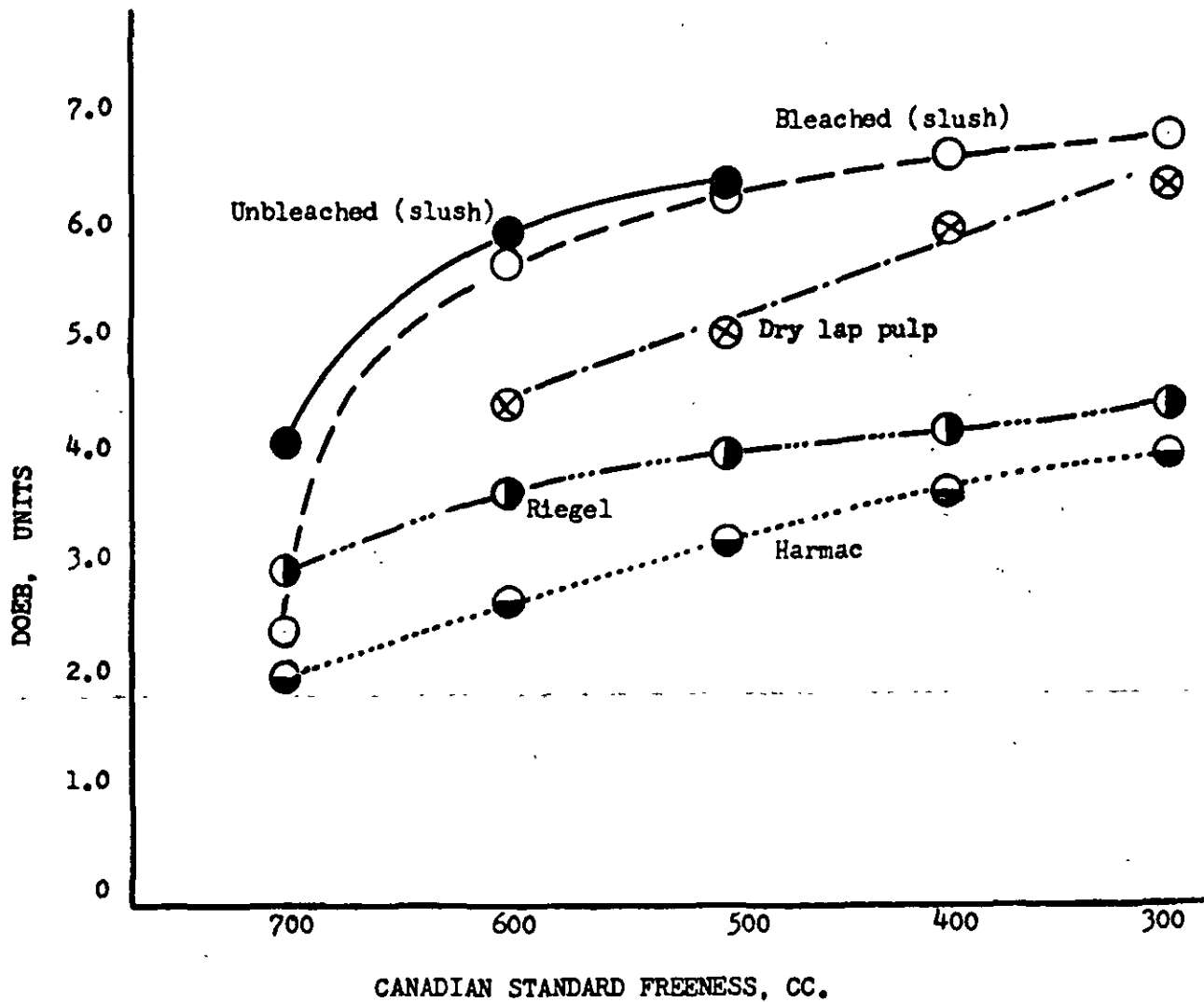
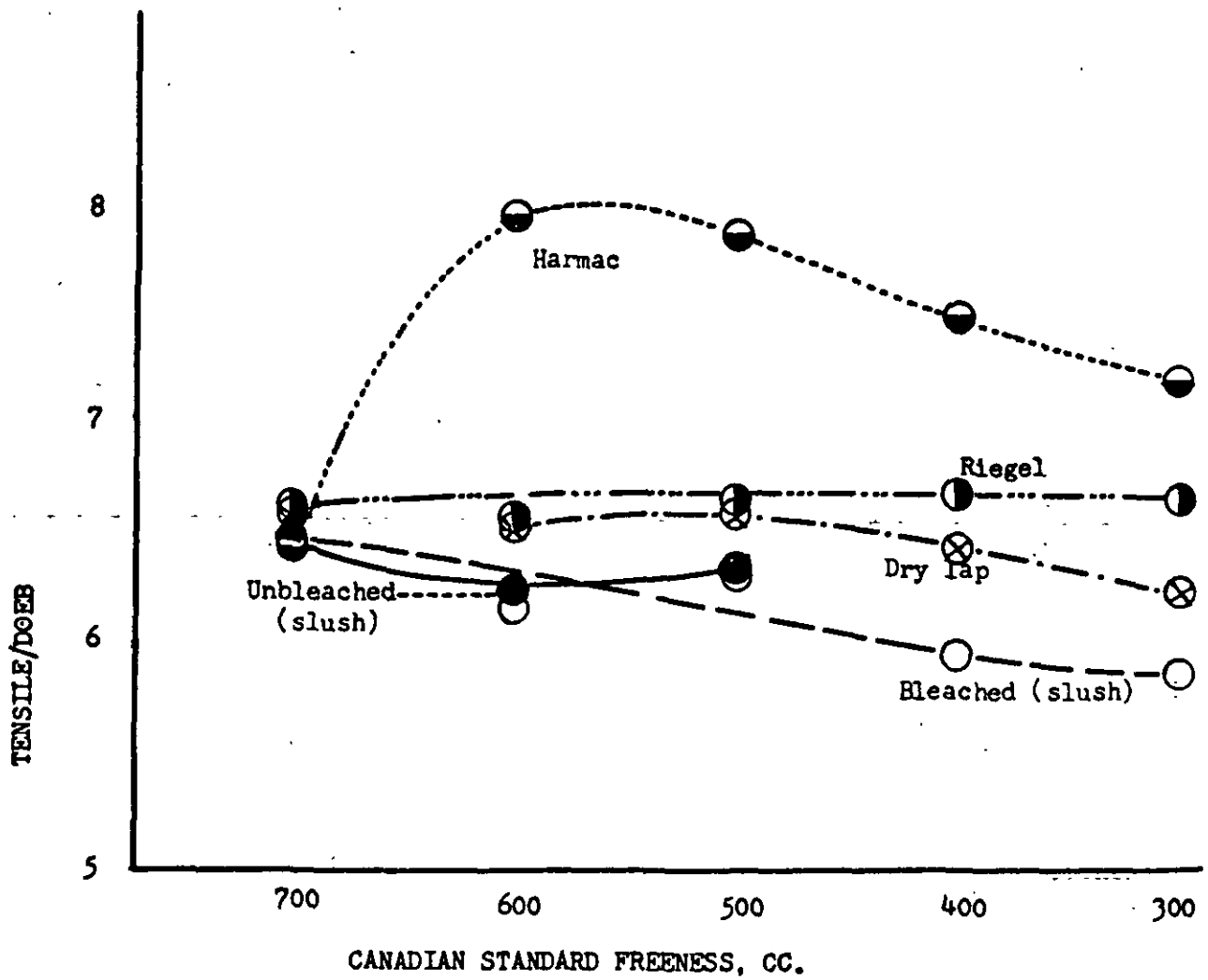


FIGURE 4

A COMPARISON OF PROPERTIES OTHER THAN BONDING AT SIMILAR FREENESS LEVELS



relation to freeness in Figure 5. Comparison of Figures 4 and 5 gives some evidence that fiber-strength probably contributed substantially to the position of the Harmac pulp in Figure 4, but that other factors, such as formation or fiber length, were also involved.

In capitulation, graphical manipulation of the handsheet strength data made possible the following estimates of the properties of the subject pulps:

(1) Very good bursting and tensile strengths of the wet St. Regis pulps could be attributed to a combination of relatively good fiber strength and exceptional fiber-to-fiber bonding.

(2) Dry lap St. Regis pulp gave evidence of having suffered substantially in bonding potential as compared to undried pulp as might be expected, and possibly had lost some fiber strength.

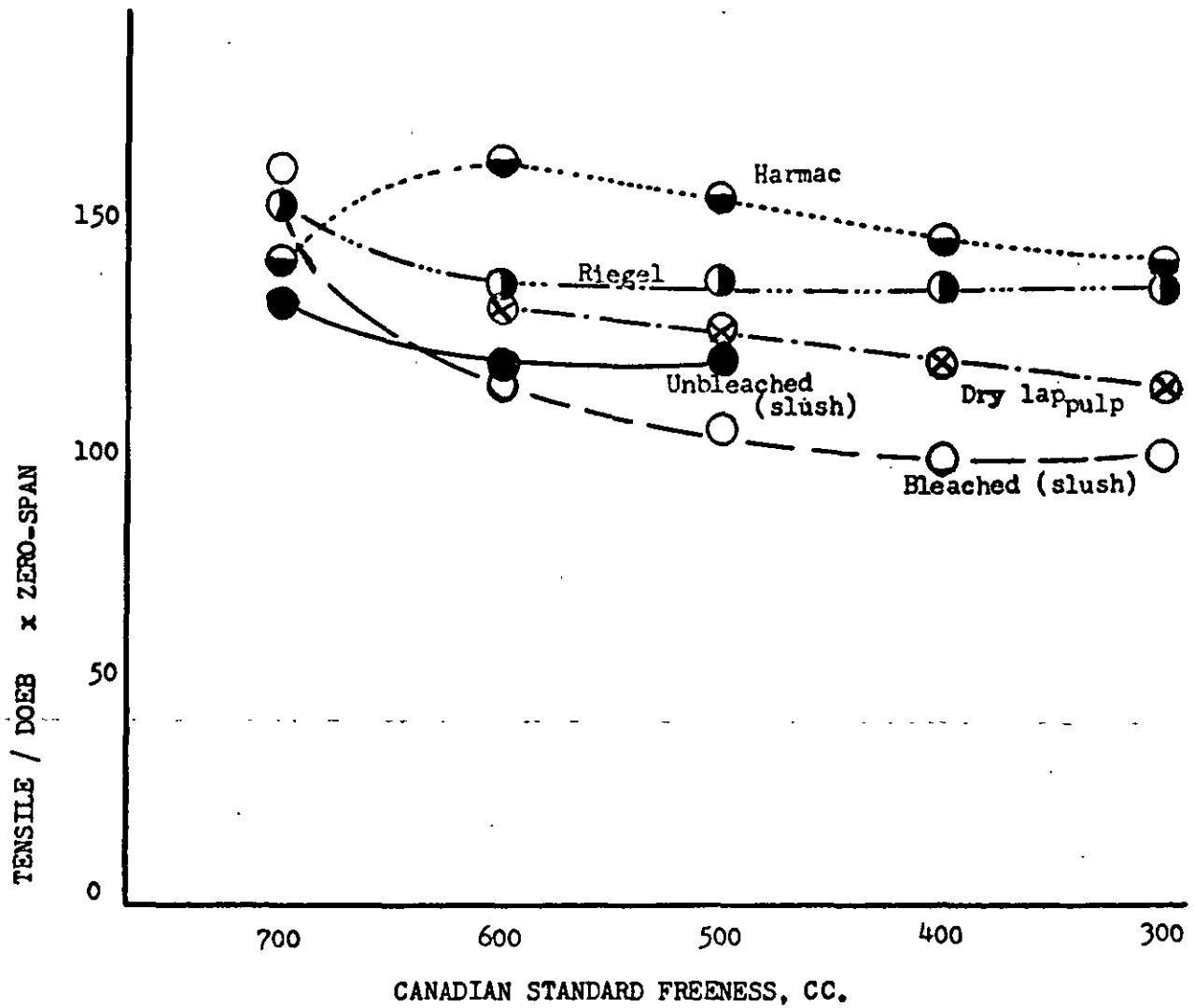
(3) Compared with a bleached Southern pine and a bleached Douglas-fir kraft dry lap pulp, the dried St. Regis pulp was outstanding in the properties which reflect fiber-to-fiber bonding. The extremely good bonding potential of the St. Regis pulp at a given beating time or freeness contributed to its lower tearing resistance at that level.

(4) The general advantage in tearing strength displayed by the Douglas-fir pulp, and to a lesser extent by the Southern pine pulp, cannot be explained by differences in fiber strength. The zero-span tensile of the St. Regis pulp is consistently higher than that of the other two pulps.

(5) Fiber lengths of the fir and pine pulps may be contributing to their advantage in tearing resistance since Isenberg (2), in his "Properties of Pulpwoods," describes the tracheid length of Southern pines to be in excess.

FIGURE 5

COMPARISON OF PROPERTIES OTHER THAN
BONDING AND INTRINSIC FIBER STRENGTH
AT SIMILAR FREENESS LEVELS



of 4.5 mm. and those of Douglas-fir as slightly less. The fiber lengths of lodgepole pine and black spruce are about 3.3 mm. However, the Douglas-fir pulp with outstanding tearing resistance has less fiber length than the Southern pine pulp. A possible explanation is that the low potential for developing fiber-to-fiber bonding which was demonstrated in the case of the Douglas-fir pulp resulted in the rupture of these bonds during the tearing test. Since the tear test value is a measure of energy consumed, the friction of the essentially unbroken fibers being pulled from their position in the sheet could have contributed substantially to the high tearing strength.

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APPENDIX

Figures A through E

Calculation of the Degree of Effective Bonding (DOEB)

APPENDIX

Calculation of the Degree of Effective Bonding (DOEB)

Studies made under Project 1513 have indicated that the relative contributions of fiber bonding and fiber strength to sheet strength properties change with the degree of bonding attained. Early in a beating cycle, sheet failure can generally be attributed to failure of the fiber-to-fiber bonds, and this factor thus controls the strength properties. As beating continues, the strength of the bonds increases and after a point, the strength of the fiber becomes the limiting factor. (Fiber length also decreases with beating and imposes still another limitation on the system, but this was not followed in the present exploratory study.)

For a series of pulps, the relative contributions of fiber strength and fiber-to-fiber bonding to sheet strength appear to be at least in part indicated by the differences in tearing resistance at a given level of tensile strength. Tearing strength (an expression of energy consumption) is adversely affected by improved bonding if the bonding results in a substantial increase in the number of fibers which break relative to those which pull out intact in the zone of failure. Thus, if a pulp exhibits a particular level of tensile strength, attained by a combination of good bonding and poor fiber strength, both of these factors contribute to poor tearing resistance by increasing the incidence of fiber breakage.

To the best of our knowledge at present, bonding is the only factor contributing to sheet strength which produces opposite effects on tensile and tearing strengths. An improvement in fiber length, fiber strength, or sheet formation should logically improve both tensile strength and tear resistance (although not necessarily to the same degree). This opposing effect may be

Calculation of the Degree of Effective Bonding (DOEB)----(Continued)

used to provide a useful relationship in making comparisons between the strength properties of several pulps.

If, as a first approximation, one assumes that, at a given level of tensile strength: (a) fiber strength, fiber length, and sheet formation have proportional effects on tearing and tensile strengths, and that (b) tensile strength is directly proportional to bonding while tearing resistance is inversely proportional to bonding, one may employ the following approximate expression:

$$t/T \propto B / 1/B \quad \text{or} \quad B \propto \sqrt{t/T}$$

where: t = tensile strength, T = tearing strength, and B = the contribution which bonding makes to sheet strength (arbitrarily called the "degree of effective bonding" or "DOEB"). In this expression, B is not an indication of total fiber bonding, but only signifies the contribution that bonding makes to tearing and tensile strengths at the particular level of tensile strength at which the computation is made.

(It should be emphasized that this so-called "degree of effective bonding" is not a fundamental expression and is not suggested as a replacement for a more fundamental expression. However, in cases such as the present study, where no other direct index of bonding is available, it appears to have considerable utility, if used with caution appropriate to the assumptions incorporated in the derivation.)

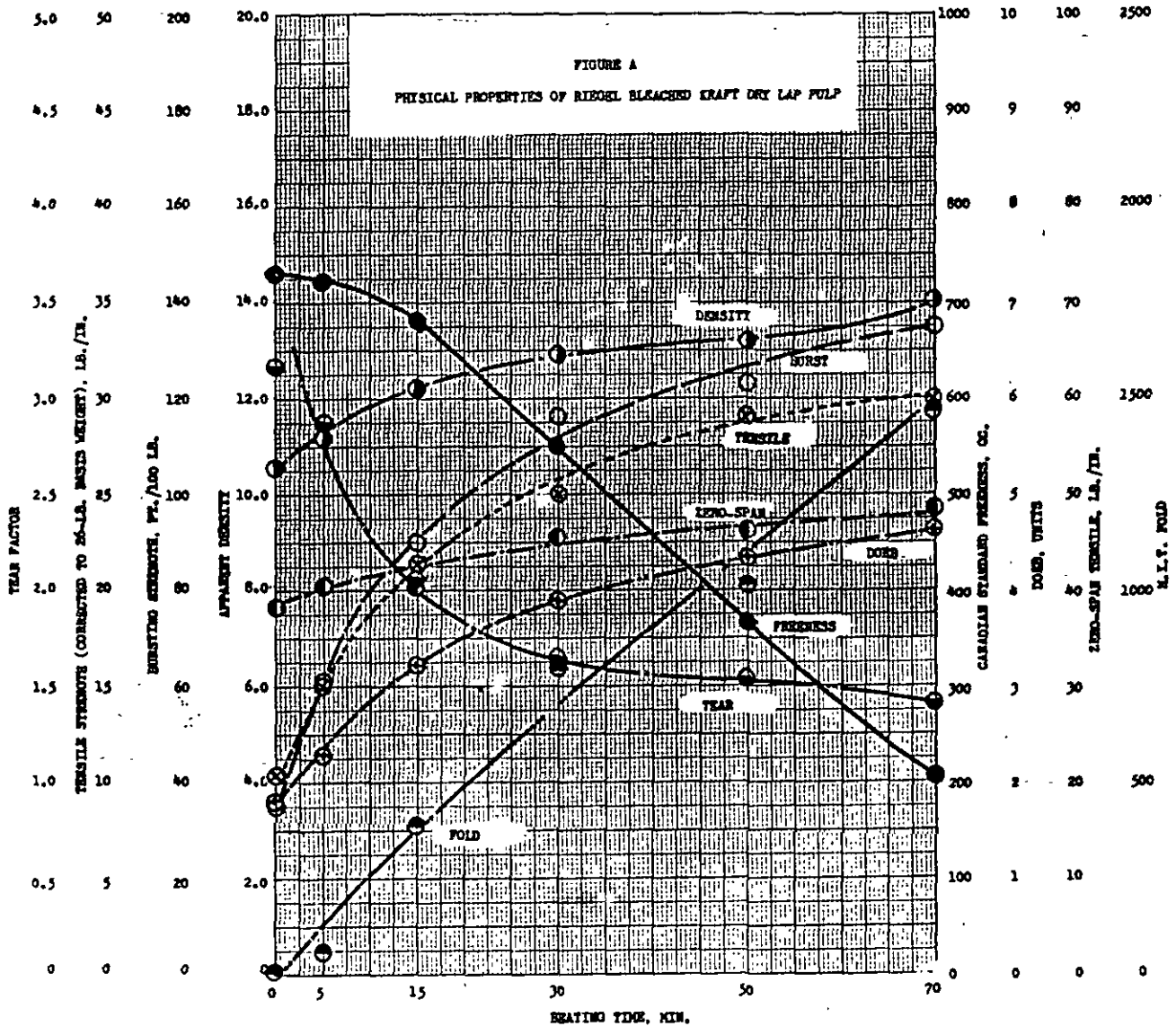
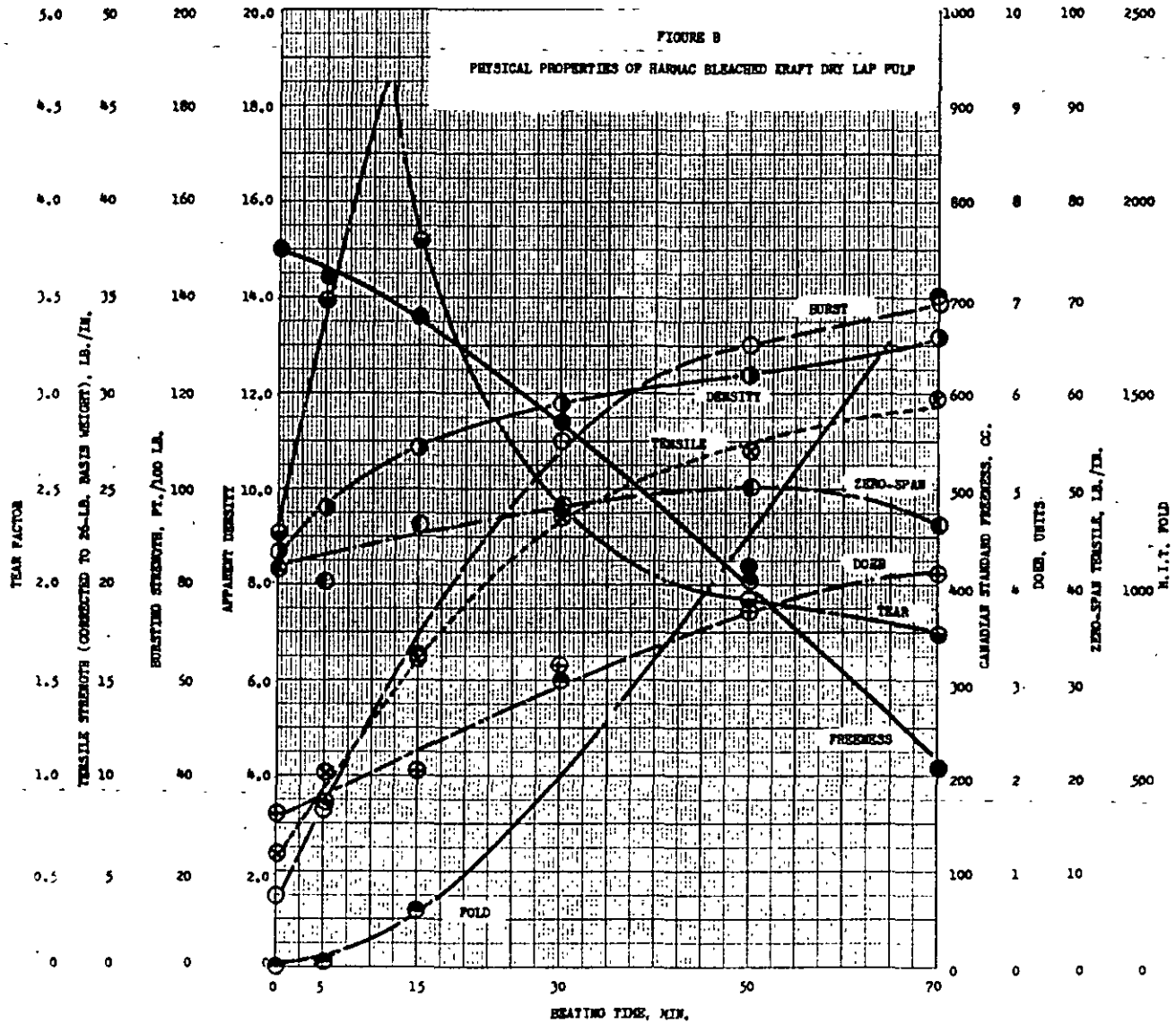
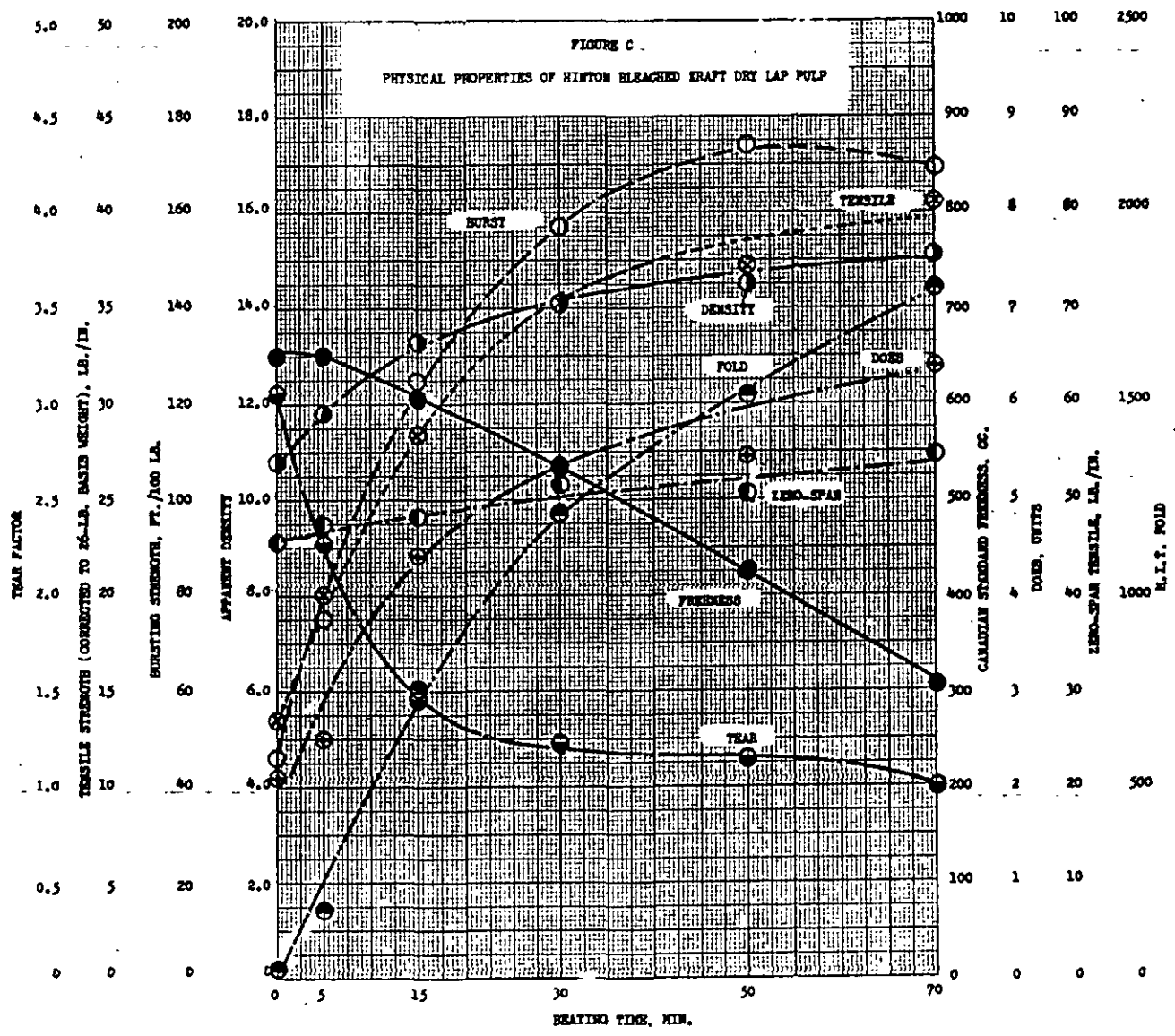
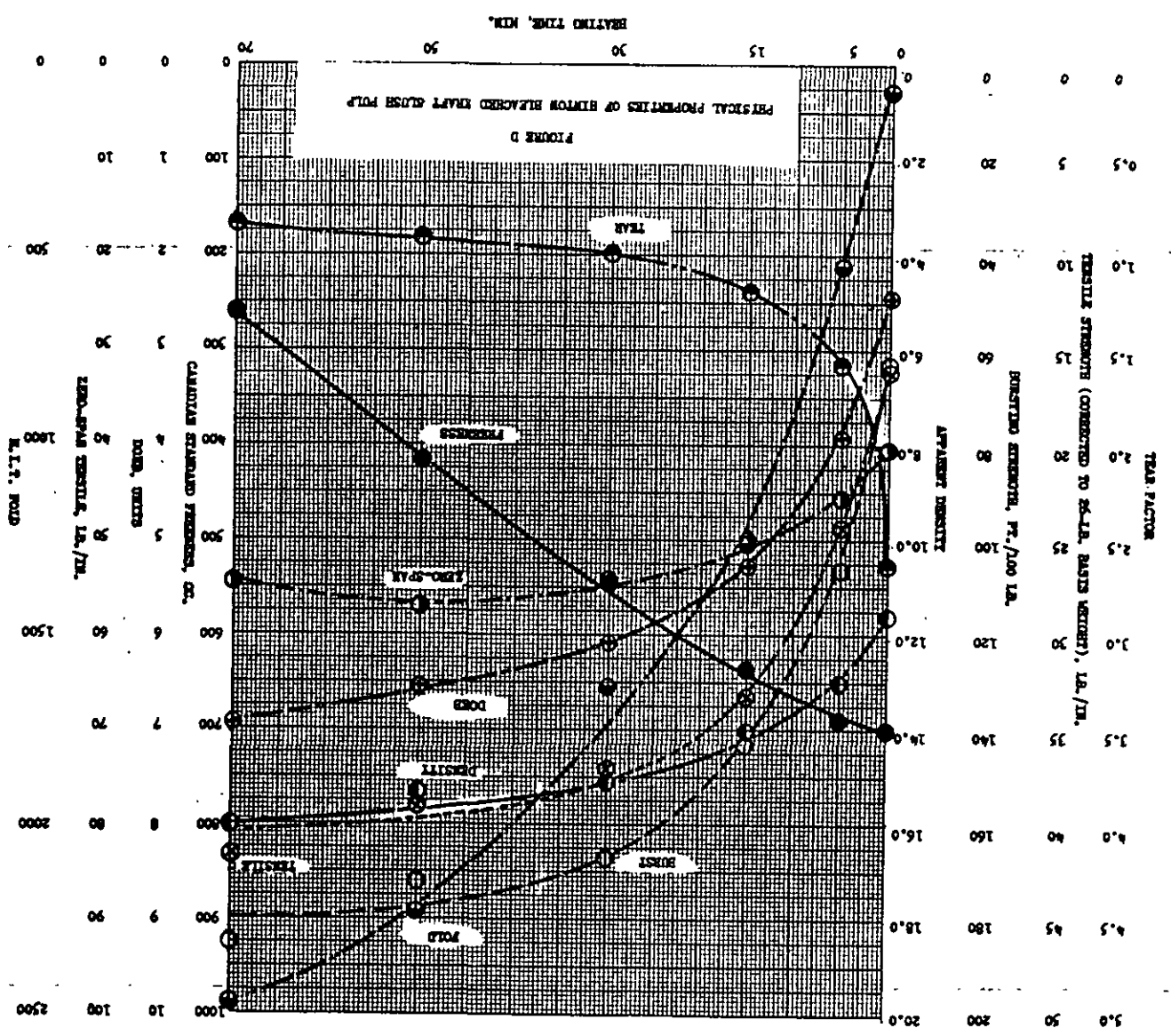
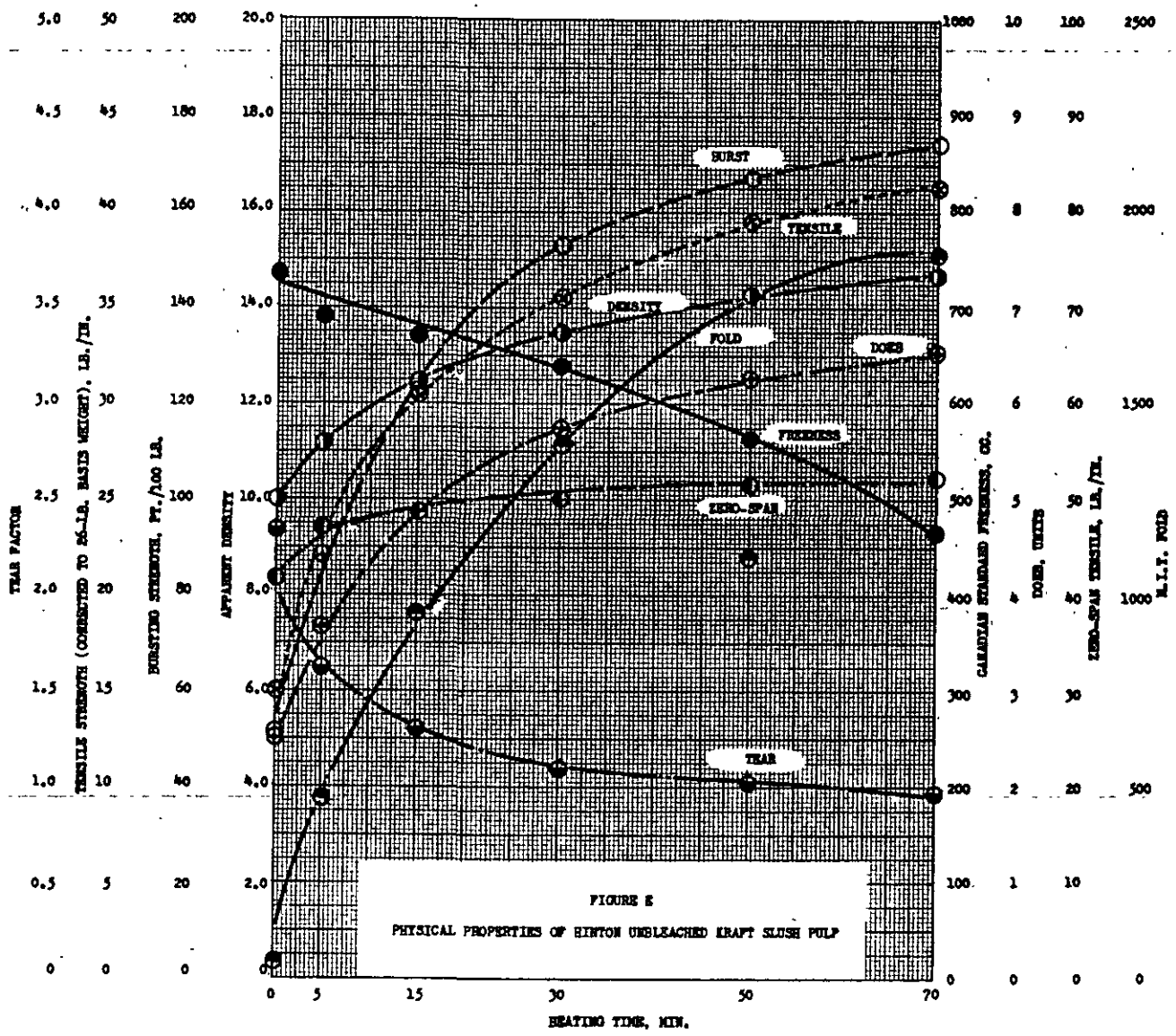


FIGURE B
 PHYSICAL PROPERTIES OF HARMAC BLEACHED KRAFT DRY LAP PULP









PROJECT REPORT FORM

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REFINING OF SOFTWOOD AND HARDWOOD KRAFT PULPS SEPARATELY AND AS MIXTURES

SUMMARY

Samples of two commercial bleached kraft pulps, one made from Southern pine and one from gumwood, were refined in a Valley beater, separately and in two component mixtures. The mixture level was maintained at 60% pine and 40% gum pulp, but the blends were made by:

- (a) Mixing the pulps before beating
- (b) Beating each pulp separately and mixing the two pulps at the same beating interval, and
- (c) Beating each pulp separately and mixing the highly beaten stock samples of one kind with lightly beaten samples of the other.

Samples taken at a number of beating intervals were formed into TAPPI Standard handsheets which were tested for bursting, tearing, and tensile strength and folding endurance.

The results obtained indicated that some small strength advantage might be obtained from beating the two kinds of pulp separately and then blending them. Some further small increase in bursting strength might possibly be obtained by beating the gum to a somewhat lower freeness

than the pins, so that the blend provides the desired freeness level. The optimum range of beating in this manner may be very narrow.

INTRODUCTION

It has often been stated that paper furnishes made up of a blend of pulps having different fiber characteristics would be improved by refining the components separately rather than as a mixture. This study was designed to investigate the effects of separate versus combined refining of a mixture of bleached Southern pine and bleached gum kraft pulps.

RAW MATERIALS

Commercially prepared bleached Southern pine kraft and bleached gum kraft obtained in dry lap form were chosen for the investigation.

DESIGN OF EXPERIMENT

Samples of the pulps were blended in the proportion of 60% softwood and 40% hardwood fiber and were refined in a Valley beater using a 5500-g. bedplate load and convenient test intervals. Additional samples of the pulps were refined separately in the same manner. Handsheets made at the several beating intervals were tested for basis weight, apparent density, bursting, tearing, and tensile strengths, and folding endurance. A third set of samples was beaten separately and sheets were made from the refined pulps at each beating interval, blended in the proportion of 60% softwood-40% hardwood fiber. The separate refining was again repeated, and this time the pulps were blended in the proportions described previously, but using

the following mixture of samples:

- (a) Pine, 5 min. refining; gum, 60 min. refining
- (b) Pine, 15 min. refining; gum, 40 min. refining
- (c) Pine, 30 min. refining; gum, 20 min. refining
- (d) Pine, 50 min. refining; gum, 5 min. refining

Handsheets were again made and tested. All of the beating, handsheet making, and testing were carried out as specified in Institute Methods 403 and 411, unless otherwise described.

DISCUSSION OF RESULTS

The results of the tests performed on the handsheets made during the beater evaluation of the separate pulps are shown in Table I. Table II contains the data concerning the handsheets made from a mixture of pine and gum pulps where both components were beaten for similar lengths of time. Figures 1-4 show these data plotted against Canadian Standard freeness.

It will be noted that the pine pulp developed burst, tensile strength, and folding endurance at a quite a steady rate, and that tearing strength decreased rapidly at first and then more slowly. The gum pulp, on the other hand, displayed steadily increasing tearing strength until late in the beating cycle. Bursting and tensile strengths were low, and folding endurance was very poor.

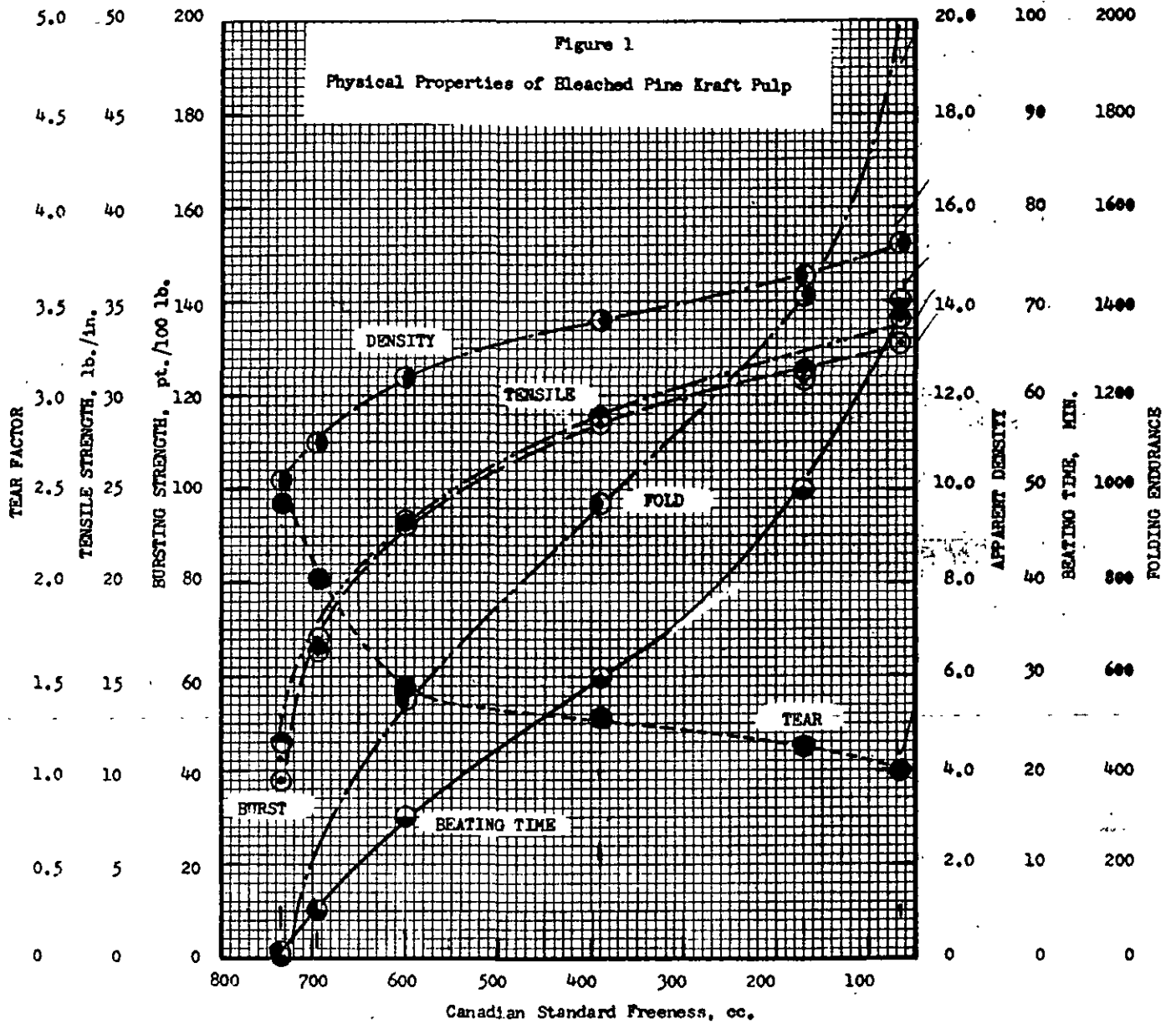
When the values for these properties are shown at two freeness levels (Table III), it is noted that only in tearing strength does the gum pulp strength approach that of the pine pulp.

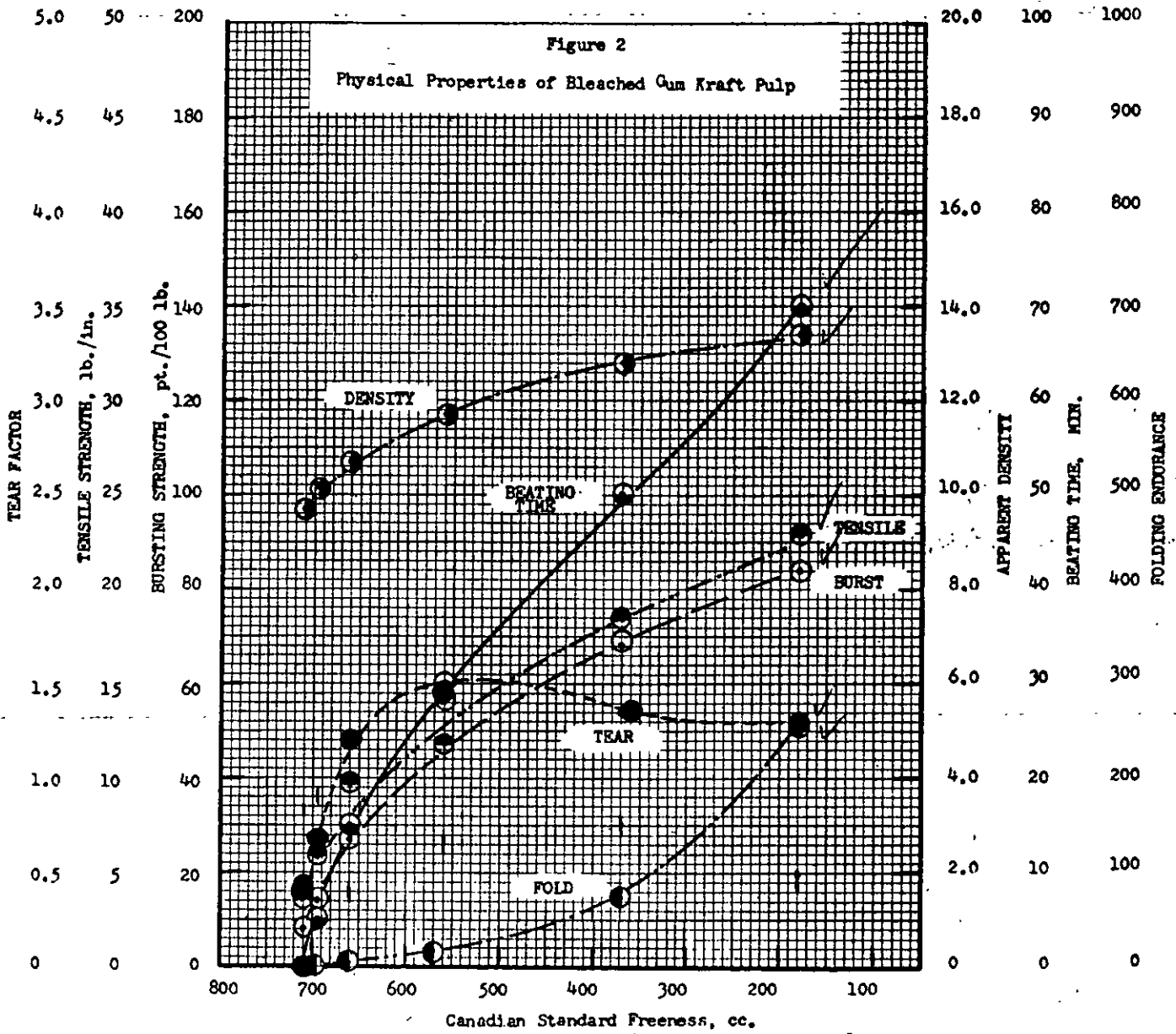
TABLE I
PHYSICAL PROPERTIES OF UNBLENDED PULPS

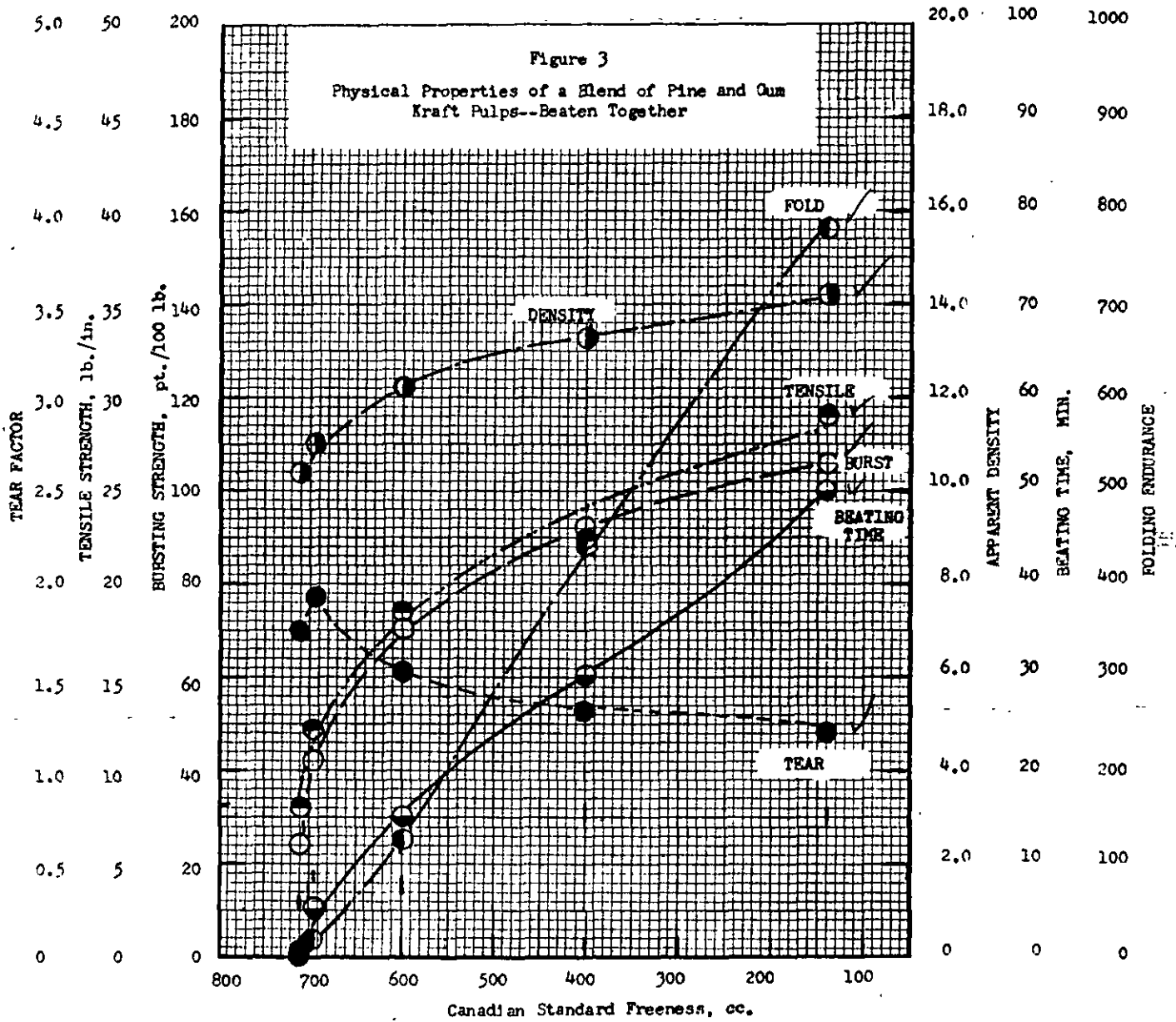
Pulp		Pine ⁽¹⁾	Oak ⁽²⁾
Canadian Standard freeness, cc.	0 ^a	735	710
	5	695	695
	15	600	660
	30	390	560
	50	170	370
	70	65	180
	Basis weight (25x40--500), lb.	0	47.5
5		46.3	46.1
15		44.8	46.1
30		47.5	46.8
50		46.4	46.0
70		48.5	45.4
Caliper, mils		0	4.7
	5	4.2	4.5
	15	3.6	4.3
	30	3.5	4.0
	50	3.3	3.6
	70	3.2	3.4
	Apparent density	0	10.1
5		11.0	10.2
15		12.4	10.7
30		13.6	11.7
50		14.1	12.8
70		15.2	13.4
Bursting strength, pt./100 lb.		0	38
	5	68	14
	15	93	27
	30	114	47
	50	123	68
	70	131	84
	Tear factor	0	2.42
5		2.01	0.67
15		1.43	1.19
30		1.28	1.45
50		1.12	1.35
70		0.99	1.28
Tensile strength, lb./in. (corrected to 45-lb. basis weight)		0	10.6
	5	16.2	5.9
	15	23.1	9.6
	30	28.8	14.2
	50	31.2	18.5
	70	34.0	22.8
	M.I.T. fold	0	14
5		99	1
15		543	3
30		968	18
50		1449	76
70		2086	254
^a Beating time, min.			

TABLE II
PHYSICAL PROPERTIES OF PULP MIXTURES

Pine, % Gum, % Method of blending		60	60
		40	40
		Before beating	After separate beating
Canadian-Standard-freeness, cc.	0 ^a	710	725
	5	695	710
	15	600	640
	30	400	485
	50	140	225
	70	--	90
Basis weight (25x40--500), lb.	0	47.7	45.6
	5	46.4	45.9
	15	46.4	42.0
	30	45.2	46.2
	50	46.9	46.9
	70	--	46.3
Caliper, mils	0	4.6	4.8
	5	4.2	4.4
	15	3.8	3.7
	30	3.4	3.6
	50	3.3	3.4
	70	--	3.1
Apparent density	0	10.4	9.5
	5	11.0	10.4
	15	12.2	11.4
	30	13.3	12.8
	50	14.2	13.8
	70	--	14.9
Bursting strength, pt./100 lb.	0	24	24
	5	42	41
	15	70	66
	30	92	89
	50	106	105
	70	--	114
Tear factor	0	1.74	1.75
	5	1.94	2.09
	15	1.53	1.62
	30	1.31	1.43
	50	1.19	1.26
	70	--	1.08
Tensile strength, lb./in. (Corrected to 45-lb. basis wt.)	0	8.0	7.2
	5	12.2	12.2
	15	18.4	15.1
	30	22.4	23.3
	50	29.1	27.7
	70	--	28.8
Folding endurance (M.I.T. fold)	0	4	3
	5	16	16
	15	124	90
	30	440	348
	50	780	851
	70	--	1287
^a Beating time, min.			







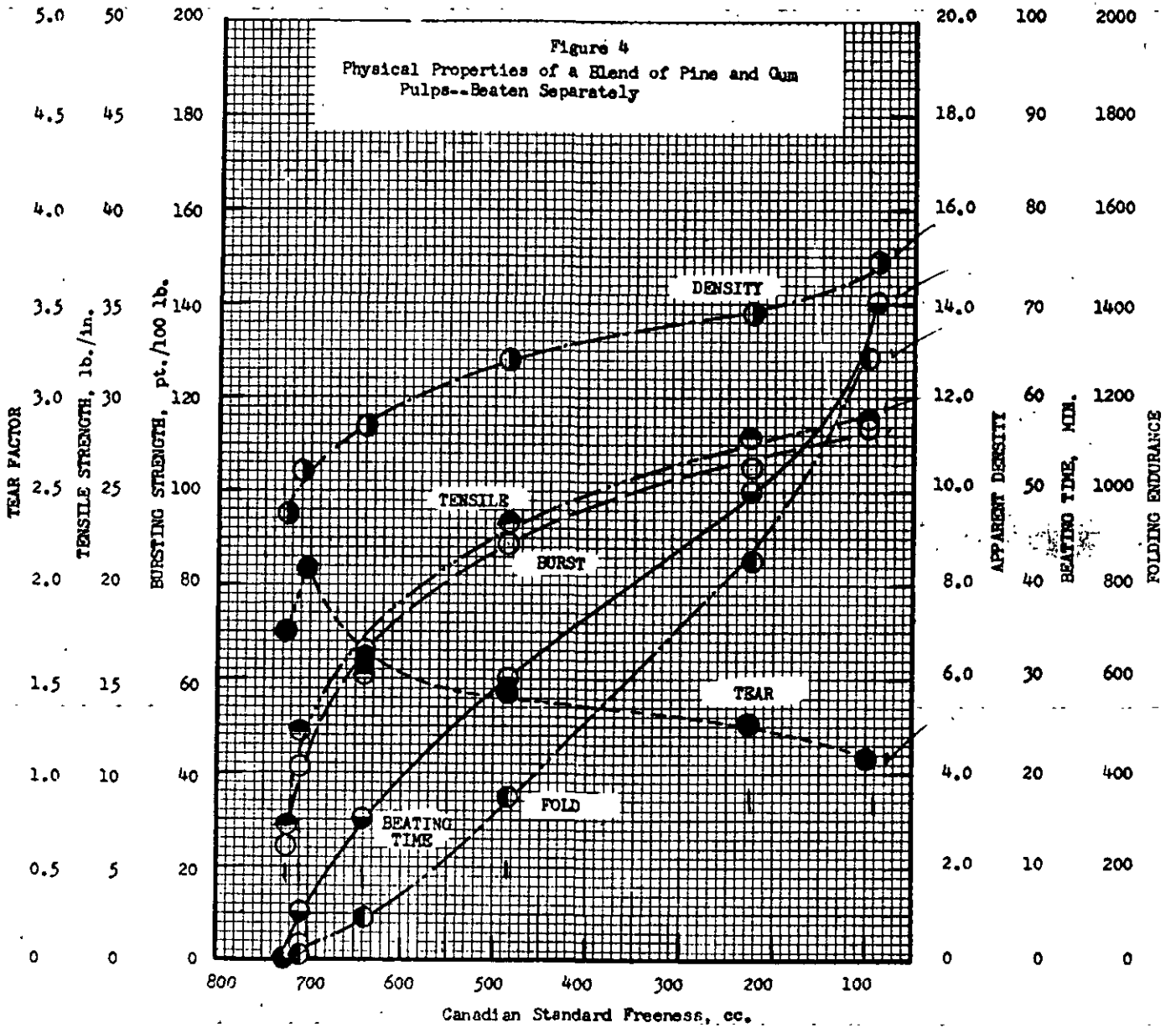


TABLE III

PHYSICAL PROPERTIES OF PULPS AT TWO FREENESS LEVELS

Composition of Handsheets	Pine	Gum	Pine-Gum Blended Before Beating	Pine-Gum Blended After Separate Beating	Predicted Values of Pine-Gum Blends ^a
<u>Properties at 600-cc. Canadian Standard Freeness</u>					
Beating time, min.	15	24	15	19	19
Apparent density	12.4	11.3	12.2	11.9	11.9
Bursting strength, pt./100 lb.	93	39	70	73	72
Tear factor	1.45	1.45	1.53	1.53	1.45
Tensile strength, ^b lb./in.	23.0	11.0	18.2	19.1	18.2
M.I.T. fold	540	13	125	140	329
<u>Properties at 400-cc. Canadian Standard Freeness</u>					
Beating time, min.	29	46	30	36	36
Apparent density	13.5	12.7	13.3	13.2	13.2
Bursting strength, pt./100 lb.	113	66	92	96	94
Tear factor	1.27	1.42	1.33	1.36	1.33
Tensile strength, ^b lb./in.	29.3	17.8	24.2	24.8	24.7
M.I.T. fold	960	65	440	510	601

^aFrom weighted average.

^bCorrected to 45-lb. basis weight.

In the same table, it can be seen that the strength of a pulp blend can be predicted very closely, if the two pulps are beaten before combining, simply by obtaining a weighted average of the strength properties at the two freeness levels. The notable exception to this is seen in folding endurance which was substantially lower for the pulp mixture than would have been forecast. When the two pulps were combined and then beaten, the strength properties were slightly lower than when the components were beaten and then blended.

In the experiment where the two pulps were beaten separately and combined at freeness levels which differed substantially for each component, (see Table IV), it is unfortunate that the freeness measurements were, in error, recorded in Schopper-Riegler instead of Canadian Standard. Rather than use a conversion chart, the Canadian freeness data for previous runs were considered and the Canadian freeness values used in Table IV are the best possible estimates of the true levels. Figures in parenthesis in this table are values taken from Figure 4 at the freeness level which characterizes each blend. Thus, it will be seen that the mixture giving the best development of burst, tensile, and fold was pine beaten 15 minutes and gum pulp beaten 40 minutes, and even that was only slightly stronger than would probably be found, were each pulp beaten to the freeness of the mixture and then combined. At all other levels of freeness the blends of pulps made at non-uniform freenesses resulted in a product inferior to blends made in other fashions. The fold values were particularly low for the mixtures made at dissimilar levels of freeness.

TABLE IV
 PHYSICAL PROPERTIES OF PULP BLENDS AT VARYING FREENESS LEVELS

Run	5A	5B	5C	5D
Pine, %	60	60	60	60
Pine beating time, min.	5	15	30	50
Pine freeness, cc. Can. Std. (est.)	695	600	390	170
cc. S.-R. (measured)	875	845	750	410
Gum, %	40	40	40	40
Gum beating time, min.	60	40	20	5
Gum freeness: cc. Can. Std. (est.)	260	460	625	700
cc. S.-R. (measured)	470	770	860	885
Mixture freeness:				
cc. Can. Std. (est.)	520	545	485	380
cc. S.-R. (measured)	815	825	790	710
Basis weight (25x40--500), lb.	44.5	46.4	44.7	43.7
Caliper, mils	3.8	3.8	3.6	3.6
Apparent density ¹	1 11.7 (12.5)	12.2 (12.3)	12.4 (12.8)	12.1 (13.3)
Bursting strength, pt./100 lb.	74 (85)	87 (81)	86 (89)	82 (98)
Tear factor ¹	1.64 (1.42)	1.47 (1.45)	1.43 (1.40)	1.42 (1.35)
Tensile strength, lb./in. ¹	19.3 (23.0)	21.4 (21.2)	21.1 (23.0)	20.0 (25.2)
(corrected to 45-lb. basis wt.)				
M.I.T. fold, double folds	132 (275)	215 (225)	201 (340)	201 (760)

¹Figures in parentheses are interpolated values taken from Figure 4 which characterize properties of beaten and blended mixtures at the Canadian Standard freeness level shown in each column.

X

PROJECT REPORT FORM

cc: The Files
Dr. May
Mr. Peckham
Dr. Jappe
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Project 1102-3
Co-op. I.P.C.
Report 14
Date December 31, 1957
Notebook 1618
Pages 47 to 112
Signed

J. R. Peckham
J. R. Peckham

THE USE OF POLYSULFIDES IN THE KRAFT PULPING PROCESS

SUMMARY

A series of experiments was performed to investigate the claim that greater yields of pulp could be realized from digestions with an alkaline liquor rich in polysulfides than from a conventional kraft cook.

Using a mixture of Southern pines for the raw material, the results of triplicate digestions indicated that unscreened yield advantages of up to 2% (based on the moisture-free wood) were possible with the polysulfide cooks. A comparison of pulp strength properties revealed that the quality of the polysulfide pulps was somewhat lower than that of the kraft pulps.

Commercial application of the polysulfide cooking procedure would apparently be dependent upon the relationship between the value of the increased pulp production and the cost of producing the polysulfide-enriched liquor. Digester corrosion would probably not be a deterrent in the consideration of the use of high polysulfide liquors, judging from the results of other investigators (2,3).

INTRODUCTION

Rene Berthier (1) has reported significant increases in pulp yields when maritime pine (Pinus pinaster) was cooked with an alkaline liquor rich in polysulfides in comparison with similar digestions using conventional kraft liquor. This study was undertaken to establish whether similar results could be obtained in pulping a mixture of Southern pines.

RAW MATERIALS

Approximately equal parts of three species of Southern pines (Long-leaf, Loblolly, and slash) were blended for the wood supply. Solutions of technical grade sodium hydroxide and purified crystals of sodium sulfide were used for the kraft liquors. Flowers of sulfur added to the sodium hydroxide solution provided the polysulfides in the so-called "soda-sulfur" cooks.

EXPERIMENTAL

The attack on this problem involved triplicate digestions using typical kraft pulping conditions and comparing the results with similar digestions when a sodium hydroxide-elemental sulfur liquor was substituted for the kraft liquor. The conditions used and the product variables obtained are shown in Table I.

The soda-sulfur liquor was prepared by dissolving 1200 grams of flowers of sulfur in 24.6 liters of a caustic solution which contained 305.6 g./l. NaOH. The mixture was heated to 50°C. and stirred occasionally. The resulting solution was analyzed for total sulfur, sodium thiosulfate, sodium sulfite, sodium sulfide, sodium polysulfides, and sodium sulfate, according

TABLE I
 COOKING CONDITIONS AND PRODUCT VARIABLES
 Polysulfide Cooking Experiments

Cook	1	2	3	Av.	4	5	6	Av.
Type of cookSoda-Sulfur.....			Kraft.....			
Sulfidity, % ¹	30.0	30.0	30.0	30.0	28.8	28.8	28.8	28.8
Permanganate no.	23.7	24.3	24.7	24.2	26.3	24.2	23.2	24.6
Yield, %								
Unscreened ²	50.3	50.3	50.7	50.4	48.6	48.7	48.7	48.7
Screened, % ²	50.0	50.0	50.2	50.1	48.2	48.1	48.0	48.1
Screenings ³	0.46	0.56	0.94	0.65	0.88	1.31	1.38	1.19

Constant conditions:

Chip charge (moisture-free basis), g.	5638
Water ratio, cc./g.	4.0
Active alkali (as Na ₂ O), % ²	17.0
Maximum temperature, °C.	170
Time to maximum temperature, min.	105
Time at maximum temperature, min.	90
Blowdown to 80 p.s.i., min.	5

¹For the soda-sulfur cooks, sulfidity was defined as:
$$\frac{\text{Total S} - (\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{SO}_4)}{\text{Active alkali}}$$

²Basis moisture-free wood.

³Basis moisture-free unscreened pulp.

Analysis of Soda-Sulfur Liquor

Total alkali, as Na ₂ O, g./l.	221
Active alkali, as Na ₂ O, g./l.	220
Sodium thiosulfate, as S, g./l.	13.25
Sodium sulfite, as S, g./l.	0.45
Sodium sulfide, as S, g./l.	11.86
Polysulfide, as S, g./l.	14.05
Sodium sulfate, as S, g./l.	1.85

Analysis of Kraft Liquor

Total alkali, as Na ₂ O, g./l.	170.5
Active alkali, as Na ₂ O, g./l.	170.5
Sulfide, as Na ₂ O, g./l.	49.1

Note: Kraft liquor analyzed using Institute Method 107-3A and 3B. Sulfidity was determined iodometrically.

Note: Soda-sulfur liquors analyzed using methods developed by the Chemical Engineering Group and reported in Progress Report Nine, Project 1568, pages 6-8.

to the methods given in the appendix. These results are summarized in Table I.

Sulfidity for the soda-sulfur cooks is defined as the ratio of "active" sulfur to active alkali, both calculated as sodium oxide. The "active" sulfur is considered to be the difference between the total sulfur analysis and the amounts of sodium thiosulfate and sodium sulfate present in the liquor and includes polysulfide sulfur. The calculation may be expressed:

$$\text{Sulfidity} = \frac{\text{Total S (as Na}_2\text{O)} - (\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{SO}_4, \text{ as Na}_2\text{O})}{\text{Active alkali (as Na}_2\text{O)}}$$

Total and active alkali were determined by Institute Method 106-3A and 3B. The normal kraft liquor, also analyzed for total and active alkali by the above method, was prepared as described in Pulping Group Procedure 40. Sulfidity for the kraft cooks was defined as the ratio of sodium sulfide to active alkali (both as Na_2O) in the usual manner.

The digester used in this work was a stainless steel vessel of 44-liter capacity, equipped for external heating and forced circulation. The chips were charged to the digester along with the desired amounts of chemical and water, and the cover was secured. At the end of the cooking cycle, the internal pressure was relieved to 80 p.s.i. and the contents of the digester were discharged through a Cyclone separator. The pulp, collected in a muslin-covered box, was transferred to a stainless steel wash tank equipped with a perforated false bottom. In washing, three dilutions were made using approximately 65 gallons of warm water in each. The first dilution was stirred for 10 minutes and the second for 5, using a Patterson Uni-power stirrer. The third dilution was not stirred. All effluent from the wash tank was directed into a muslin-

covered wash box, and entrained fibers were returned to the pulp mass. Screening was carried out on a small Valley flat screen fitted with 0.010-in. slotted plates. The rejected portion of the pulp was oven dried, weighed, and discarded. The weight appears as "screenings" in the yield figures and is reported as a percentage of the unscreened pulp.

The accepted pulp was caught in a tank identical with the wash tank and was partially dewatered by draining the tank. The effluent from the tank was treated as described for the washing process to minimize loss of fines. The partially dewatered stock was transferred to a laundry-type centrifuge which was lined with a coarse screen. The first effluent from the centrifuge was passed through the pulp cake to retain fines. The cake of pulp removed from the centrifuge was broken into bits in a mechanical device designed for this purpose, and the crumbs were packaged in polyethylene bags. Representative samples removed at this time were weighed, oven dried at 105°C., and reweighed to establish the moisture content of the pulp. From these data the yield of pulp, based on moisture-free wood, was determined.

The unbleached pulps were beater evaluated, using Institute Methods 403 and 411. The results of these tests are shown in Table II.

The bleaching characteristics of the six pulps were investigated by subjecting them to a 3-stage bleaching sequence. This was done by applying the same amount of chlorine to each pulp in a chlorination stage, extracting with sodium hydroxide, and applying a bleachability test to the chlorinated and extracted pulps. The data concerning these experiments appear in Table III.

TABLE II

BLEACHING CONDITIONS AND PRODUCT VARIABLES
 Polysulfide Cooking Experiments

Cook Type of cook	1	2	3	Av.	4	5	6	Av.
Soda-Sulfur.....			Kraft.....			
<u>CHLORINATION</u>								
Residual Cl ₂ (basis Cl ₂ applied), %	13.9	20.8	3.5	12.7	14.3	14.8	16.6	15.2
<u>CAUSTIC EXTRACTION</u>								
Yield after chlorination and extraction, % ¹	94.4	93.5	93.7	93.9	94.1	93.7	92.9	93.6
<u>HYPOCHLORITE BLEACHABILITIES</u>								
Hypochlorite required to reach 80% G.E. brightness, %	2.12	2.16	2.29	2.19	2.30	2.24	2.10	2.21
Total chlorine to 80 G.E. brightness, % ¹	10.7	10.1	11.9	10.9	10.9	10.8	10.4	10.7
<u>CONSTANT CONDITIONS:</u>								
Chlorinations:	Chlorine applied, %			10.0				
	Temperature, °C.			20				
	Consistency, %			3.0				
	Retention time, min.			60				
Caustic Extractions:	NaOH applied, %			3.0				
	Temperature, °C.			40				
	Consistency, %			10.0				
	Time, min.			60				
Hypochlorite Bleachabilities:	Consistency, %			10.0				
	Temperature, °C.			38				
	Time, hr.			4.0				

¹Basis unbleached pulp.

TABLE III
 PHYSICAL PROPERTIES OF UNBLEACHED PULPS

Cook		1	2	3	4	5	6
Schopper-Riegler freeness, cc.	0 ^a	885	890	890	885	890	895
	5	880	880	890	885	890	890
	15	850	865	870	860	870	870
	30	785	780	775	810	800	805
	50	470	475	475	530	535	570
	70	235	220	249	285	305	300
Basis weight (25x40-- 500), lb.	0	44.4	45.4	43.0	43.3	42.7	45.8
	5	44.8	45.9	43.9	45.3	45.8	45.6
	15	44.8	45.4	43.8	45.7	44.8	44.1
	30	44.2	43.4	44.4	45.1	45.3	45.3
	50	47.2	44.8	43.7	43.6	44.8	44.4
	70	44.5	46.9	44.4	46.4	46.8	47.4
Caliper, mils	0	5.2	5.1	5.0	5.4	5.2	5.1
	5	4.8	4.7	4.7	5.0	4.9	4.7
	15	4.1	4.1	4.1	4.3	4.1	4.1
	30	3.8	3.6	3.8	3.8	3.8	3.8
	50	3.6	3.4	3.4	3.4	3.5	3.5
	70	3.2	3.4	3.3	3.4	3.4	3.5
Apparent density	0	8.5	8.9	8.6	8.0	8.2	9.0
	5	9.3	9.8	9.3	9.1	9.3	9.7
	15	10.9	11.1	10.7	10.6	10.9	10.8
	30	11.6	12.1	11.7	11.9	11.9	11.9
	50	13.1	13.2	12.9	12.8	12.8	12.7
	70	13.9	13.8	13.5	13.6	13.8	13.5
Bursting strength, pt./100 lb.	0	30	34	33	26	25	30
	5	58	65	62	59	57	56
	15	103	109	108	104	102	104
	30	127	127	136	134	136	136
	50	147	147	145	157	153	144
	70	150	137	151	150	148	159
Tear factor	0	3.54	3.72	3.49	3.44	2.93	3.54
	5	3.84	3.42	3.62	4.00	3.69	4.25
	15	2.14	2.05	2.05	2.39	2.46	2.36
	30	1.74	1.59	1.71	1.82	1.85	1.92
	50	1.42	1.43	1.37	1.43	1.47	1.60
	70	1.10	1.22	1.22	1.27	1.30	1.43
Tensile strength, lb./in.	0	11.7	11.8	9.9	10.4	9.1	11.5
	5	15.2	17.9	14.8	16.2	16.4	19.9
	15	25.6	27.0	24.2	25.7	23.2	27.3
	30	32.5	32.6	30.1	32.5	32.1	33.6
	50	35.1	34.2	33.7	35.9	35.1	36.8
	70	33.6	36.8	37.5	36.1	34.3	37.9
M.I.T. fold	0	12	16	12	14	11	21

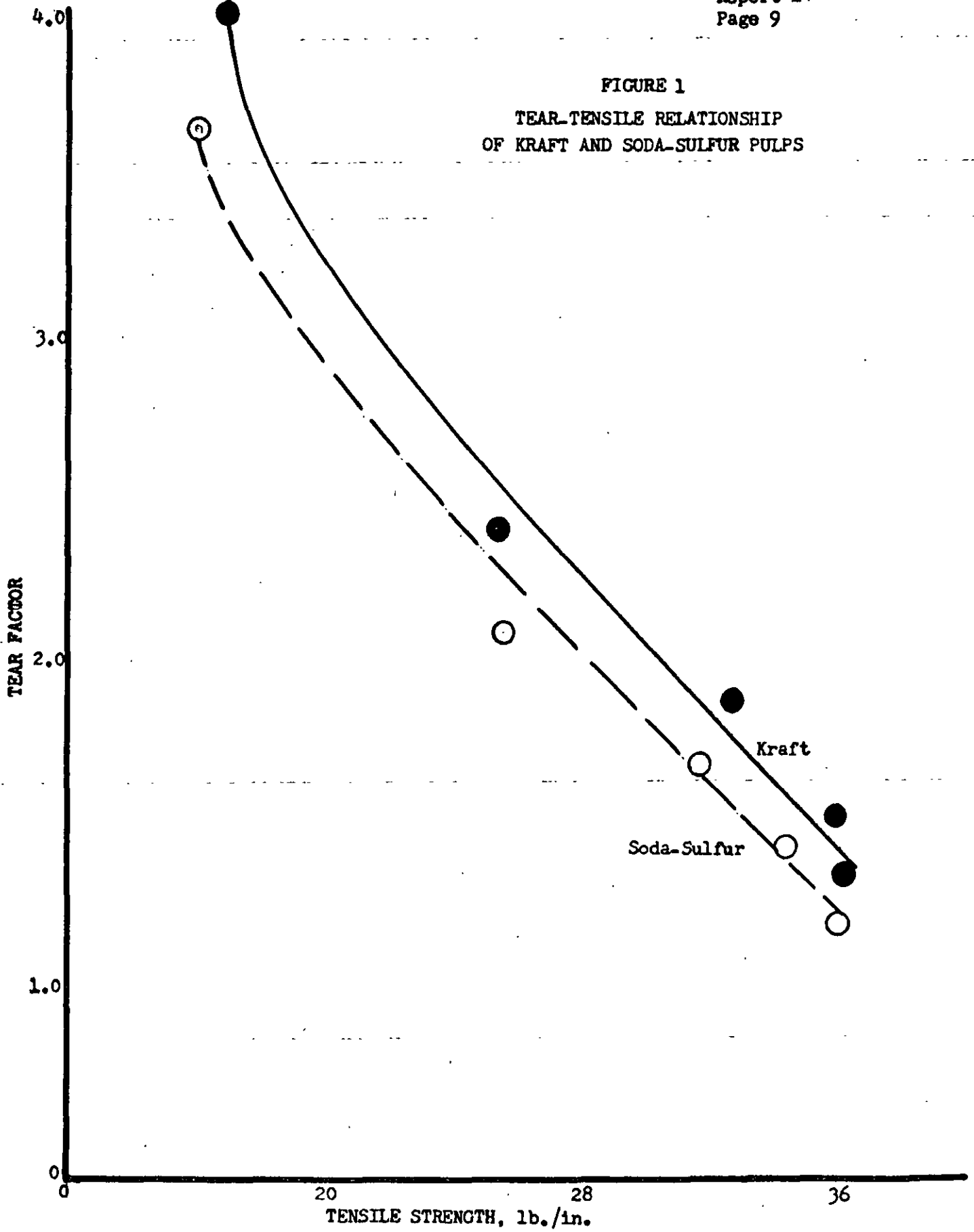
DISCUSSION OF RESULTS

The digestions made with sodium hydroxide and sulfur (Cooks 1-3) were specially designed to have a high polysulfide content as compared with the regular kraft Cooks 4-6. The permanganate number for the soda-sulfur pulps averaged 24.2 and for the kraft cooks, 24.6. At this permanganate number, an average unscreened yield of 50.4% was obtained for soda-sulfur pulps and 48.6% for kraft pulps. Screening rejects were lowest for the soda-sulfur pulps, 0.65 as compared to 1.19% for the kraft pulps.

The pulps were essentially the same color and behaved similarly when bleached. The soda-sulfur pulps consumed a total of 10.9% chlorine to achieve a brightness of 80% G.E. The average for the kraft pulps was 10.7.

The pulp strength data shown in Table IV were plotted against beating time in Figures A through F in the appendix. Table IV shows the results obtained when the various pulp properties were compared at two freeness levels. Figure 1 compares the two kinds of pulps when the tearing strength is plotted against tensile strength. From these data it would appear that kraft pulps are somewhat superior to soda-sulfur pulps, especially in bursting and tensile strengths and folding endurance. The differences are more striking at the 700-cc. freeness level than they are at 400-cc. freeness. The several strength differences indicate that the soda-sulfur cook reduces not only the bonding potential but also the strength of the individual fibers. The strength differences would not, however, be classified as major.

FIGURE 1
TEAR-TENSILE RELATIONSHIP
OF KRAFT AND SODA-SULFUR PULPS



The desirability of pulping with polysulfide-rich liquors is dependent upon several factors. The yield advantage, which was demonstrated experimentally, is offset to some extent by the need for a modified recovery system which would produce a soda liquor and elemental sulfur (or one in which the sulfur is not recovered). In addition, Berthier noted that corrosion of iron vessels might be expected from this type of cooking liquor.

Waiving consideration of the latter factor momentarily, the polysulfide (or soda-sulfur cook as we will hereafter term it) system can be compared with a conventional kraft system to determine whether the expected yield advantage would justify the necessary modification of the kraft mill.

Assuming that a 2% yield increase (based on wood charged to the digester) can be realized, a soda-sulfur system in a 300-ton mill would result in a production of 312 tons of pulp ($300/48 \times 50$). This represents an advantage of about \$1400/day (based on average price of unbleached kraft pulp). Offsetting this is an increased demand for sulfur since, to produce polysulfides in a liquor equal to the sulfidity afforded conventionally by the monosulfide, an excess of sulfur must be provided to take care of the unavoidable formation of sulfate and thiosulfate. Analysis of the soda-sulfur white liquor, shown in Table I, indicates that for each 100 lb. of sulfur present in the active form, 30.7 lb. of sulfur would be required in the form of sulfate and thiosulfate. (It should be emphasized at this point that the experimental soda-sulfur liquor was made with no intent or effort to minimize thiosulfate formation. Whether or not an optimum set of conditions would afford savings in this direction is not known.) Therefore, a mill processing 624 tons of wood to produce 312 tons of

TABLE IV

COMPARISON OF PHYSICAL PROPERTIES
 OF KRAFT AND SODA-SULFUR PULPS

Cook Type of cook	1	2	3	Av.	4	5	6	Av.
	...Soda-Sulfur.....			Kraft.....			
<u>Properties at 700-cc. Schopper-Riegler Freeness</u>								
Beating time, min.	36	37	37	37	37.5	39.5	40.5	39.2
Apparent density	12.3	12.6	12.3	12.4	12.3	12.4	12.4	12.4
Bursting strength, pt./100 lb.	135	142	142	140	146	148	145	146
Tear factor	1.62	1.52	1.40	1.51	1.64	1.63	1.72	1.66
Tensile strength, lb./in.	33.2	33.5	31.7	32.8	34.1	34.3	35.6	34.7
Zero-span tensile, lb./in.	52.0	57.2	48.5	52.6	50.4	56.3	49.0	51.9
Ratio, tensile:zero-span	0.64	0.58	0.65	0.62	0.70	0.61	0.72	0.68
Folding endurance, double folds	583	622	730	645	1155	1022	1030	1069
<u>Properties at 400-cc. Schopper-Riegler Freeness</u>								
Beating time, min.	55	53.5	54.5	54	58.5	60.5	62	60.5
Apparent density	13.3	13.4	13.1	13.3	13.2	13.3	13.1	13.2
Bursting strength, pt./100 lb.	148	147	149	148	158	154	154	155
Tear factor	1.33	1.40	1.32	1.35	1.34	1.37	1.47	1.39
Tensile strength, lb./in.	35.2	34.8	35.0	35.0	36.2	35.0	37.6	36.6
Zero-span tensile, lb./in.	52.0	57.2	48.5	52.6	47.4	56.1	49.0	50.8
Ratio, tensile:zero-span	0.68	0.61	0.72	0.67	0.76	0.62	0.77	0.72
Folding endurance, double folds	853	853	1000	902	1430	1250	1550	1410

pulp, using the cooking conditions practiced in these experiments, would charge (during a single 24-hr. period) active alkali amounting to 17% of 624 tons, or 106.08 tons (Na_2O basis). Assuming a sulfidity of 30%, 31.82 tons of sulfur compounds (as Na_2O) would be present. The sulfur contained in these compounds would be $41.18/62 \times 32$ or 16.42 tons of sulfur/day. In order to satisfy the sulfur requirements of the soda-sulfur liquor, the sulfur actually used would amount to 21.25 tons $\times 130.7\%$ or 21.46 tons per day.

If the recovery system were operated in such a fashion that the sulfur would be entirely lost from the system, then (assuming a price of \$32/ton for sulfur), sulfur make-up would cost about \$687/day. This would leave a net advantage of about \$713/day for the 300 ton mill.

Because of the obvious economic and pollution problems posed by the elimination of sulfur compounds from the recovery smelt, a system which would bring the sulfur back into the operation would be desirable. Since polysulfides are converted to the monosulfide in the digester, the black liquor would be comparable to a kraft black liquor in all respects except for the higher level of thiosulfate content and a lower ratio of organic to inorganic matter. This liquor could be concentrated in the conventional manner and burned in the recovery furnace. The smelt would then be composed primarily of sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S). Dilution with water would result in a typical kraft green liquor. To remove the Na_2S , a stripping tower could be employed using carbon dioxide (probably obtained from the lime kiln) to convert the Na_2S to H_2S . The H_2S gases given off could be further treated by the Chance-Claus process with air in the presence of a catalyst

(Fe_2O_3 or activated charcoal), to produce elemental sulfur and water. The green liquor, freed of the sulfur compounds, would be causticized in the usual manner. The resulting sodium hydroxide solution could be mixed with the elemental sulfur to produce the soda-sulfur cooking liquor.

The costs involved in this recovery are extremely difficult to predict. There are three steps proposed which are not necessary in a conventional kraft recovery, all of which would mean additional expense since none of the usual stages are eliminated. Problems connected with the conversion of the H_2S gas to elemental sulfur and the preparation of the soda-sulfur liquor to obtain the maximum polysulfide content are difficult to evaluate at this time. However, if sulfur could be recovered at a cost less than the delivered price of purchased sulfur, the difference would be added to the previously suggested monetary advantage of \$713/day for a 300-ton mill.

The digester corrosion cited by Berthier seems to be refuted to some extent by work reported by Hassler (2) and Dela Grange (3) in 1955. The experience of the West Virginia Pulp and Paper Company in their Tyrone plant was cited to prove that a soda-sulfur liquor was much less corrosive than one containing monosulfide only. Even mixing sulfur and a solution containing monosulfide acted to make the latter less corrosive. It was stated that polysulfides in very small amounts may be harmful, but if the percentage is quite high, they seem to inhibit the reaction with the metal of the digester. It was recommended that the polysulfides be added at the caustizer.

CONCLUSIONS

The presence of polysulfides in alkaline cooking liquors was found to increase the unscreened yield from Southern pine chips by about 1.7%. The screened yield advantage was 2% because of the fewer screenings in the polysulfide pulp.

The polysulfide pulp had the same characteristic color as the kraft pulp and bleaching resistance was the same.

The pulp strength properties of the polysulfide pulps were somewhat inferior to those of the regular kraft pulps.

LITERATURE CITED

- (1) Berthier, René. Assoc. Technique de l'Industrie Papetiere Bull. No. 4: 93-106(1953).
- (2) Delà Grange, Louis A. Tappi 38, no. 6:347-352(June, 1955).
- (3) Hassler, John W. Tappi 38, no. 6:265-274(May, 1955).

APPENDIX I

METHODS FOR ANALYSIS OF POLYSULFIDE LIQUORS

The methods used for most of the analyses can be found on pages 6-8 of Progress Report Nine, Project 1568. A special method covering the analysis of polysulfide sulfur appears below:

The basic reaction is $\text{Na}_2\text{S}_n + (n-1) \text{Na}_2\text{SO}_3 = \text{Na}_2\text{S} + (n-1) \text{Na}_2\text{S}_2\text{O}_3$.

Procedure

To a 10-ml. sample of the original liquor, an excess of 0.4 N Na_2SO_3 (50 ml.) is added and heated on a steam bath at 50°C. for 15 minutes or until the yellow color disappears. Transfer the treated sample to a 500-ml. volumetric flask and add a 30-ml. 0.88 M Zn acetate-30 ml. 1.88 M Na_2CO_3 suspension to remove sulfide; dilute to volume. Filter on #40 Whatman. Remove a 25-ml. aliquot (0.5 ml. of original liquor). Add 3 ml. formaldehyde to inactivate excess Na_2SO_3 . After acidification with acetic acid, the thiosulfate is determined by the usual iodometric titration. The thiosulfate from this titration comprises the amount formed from the polysulfides as well as that originally present in the liquor. Therefore, the original thiosulfate is determined by the same method excluding the Na_2SO_3 treatment. The difference between the two titrations denotes the thiosulfate formed from the polysulfides, which can be calculated as polysulfide sulfur.

APPENDIX II

Figures A-F

Physical Properties of Cooks 1-6, respectively

FIGURE A
PHYSICAL PROPERTIES OF COOK 1

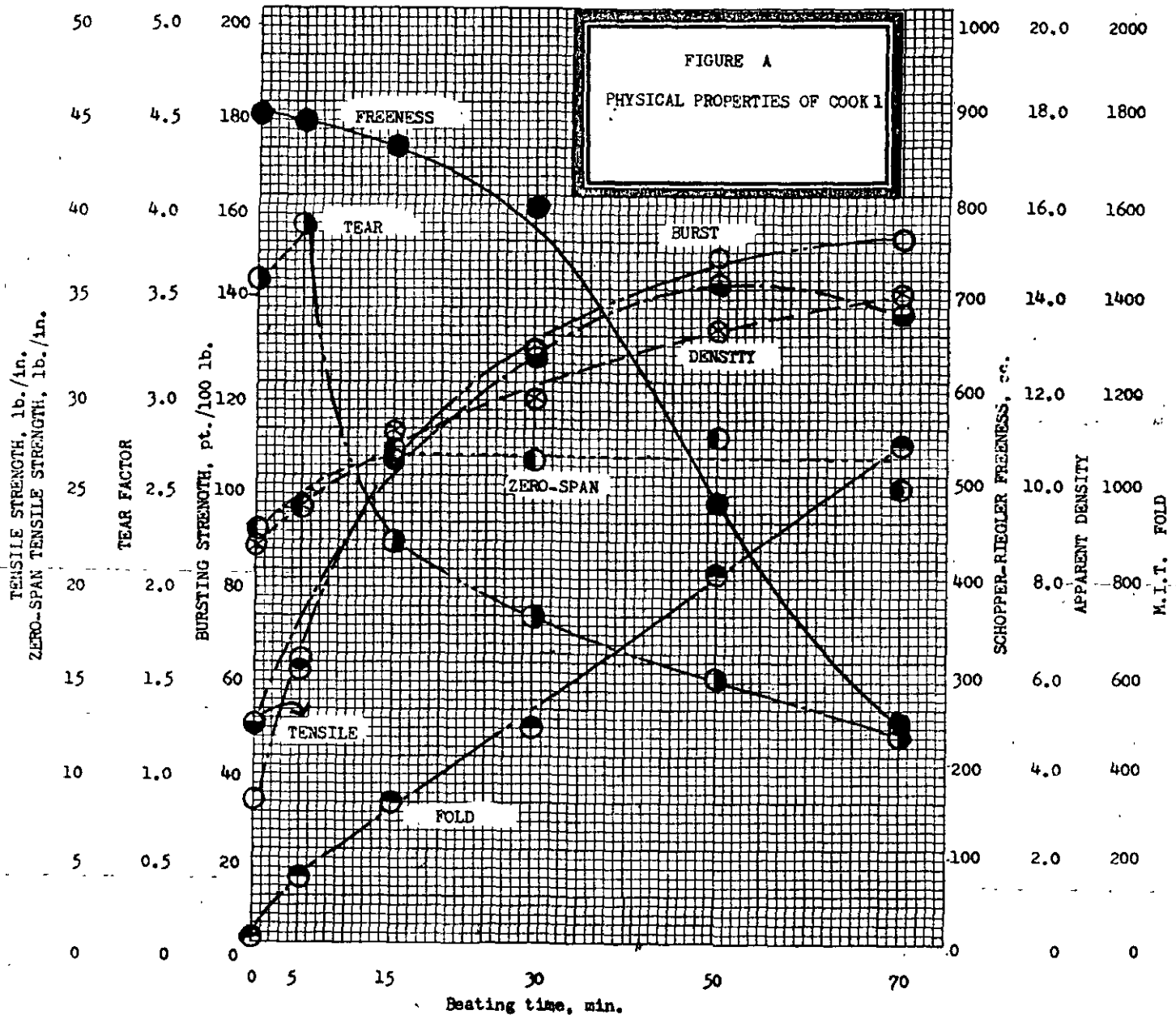


FIGURE B
PHYSICAL PROPERTIES OF COOK 2

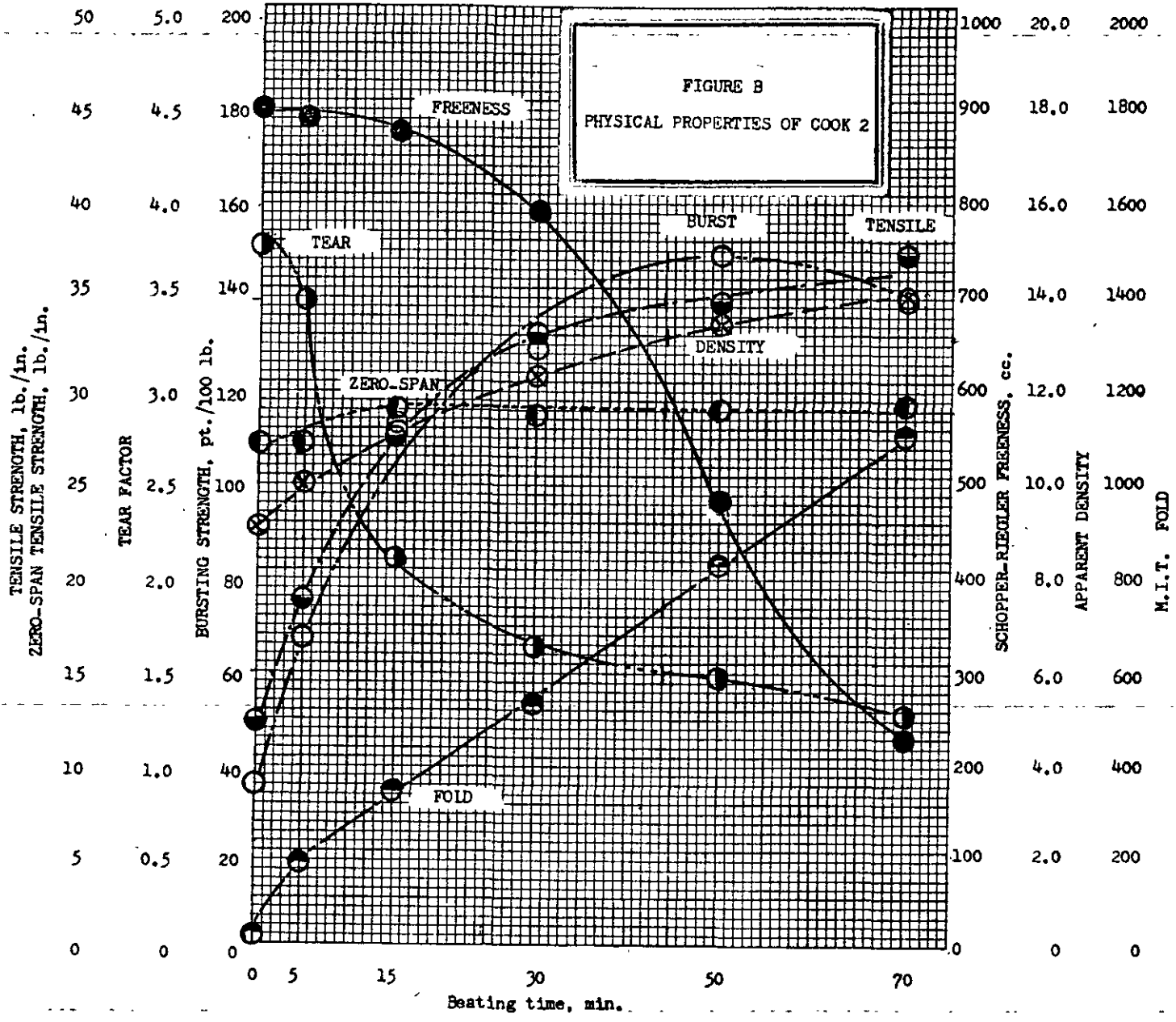


FIGURE C
PHYSICAL PROPERTIES OF COOK 3

